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AVAILABILITY OF SEDIMENT-ADSORBED HEAVY METALS TO BENTHOS WITH --ETC(U)
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LEVEL ¹² DREDGED MATERIAL RESEARCH PROGRAM



TECHNICAL REPORT D-78-42

AVAILABILITY OF SEDIMENT-ADSORBED HEAVY METALS TO BENTHOS WITH PARTICULAR EMPHASIS ON DEPOSIT-FEEDING INFAUNA

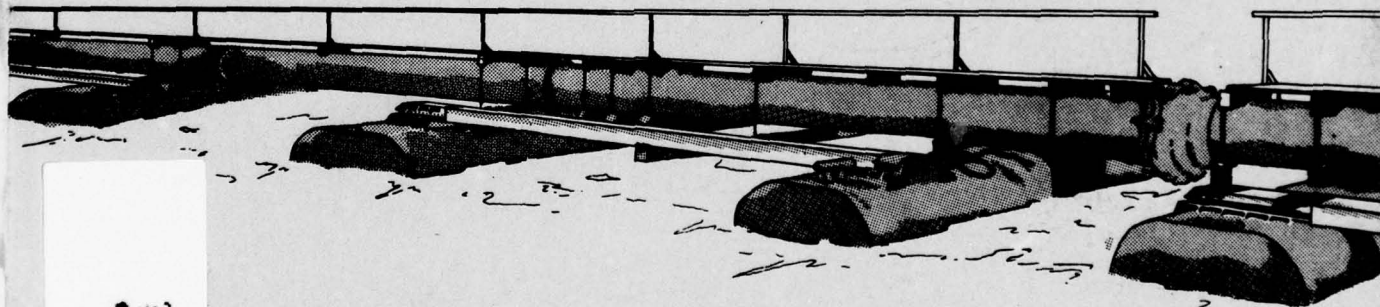
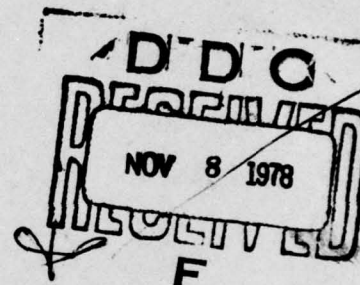
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August 1978

Final Report

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IN REPLY REFER TO: WESEV

30 September 1978

SUBJECT: Transmittal of Technical Report D-78-42

TO: All Report Recipients

1. This technical report presents the results of research undertaken as Work Unit 1D06 of Task 1D, Effects of Dredging and Disposal on Aquatic Organisms, of the Corps of Engineers' Dredged Material Research Program. Task 1D was a part of the Environmental Impacts and Criteria Development Project (EICDP), which had a general objective of determining on a regional basis the direct and indirect effects on aquatic organisms due to dredging and disposal operations. The study reported on herein was a part of a series of research contracts developed to achieve the EICDP general objective.

2. The purposes of this study were to determine the bioavailability of sediment-associated heavy metals to benthic invertebrates and to determine the degree of correlation between tissue concentration and metals concentration in various chemical extractants from the sediments. Animals were exposed to contaminated sediments for up to six weeks.

3. A total of 136 species-sediment-metal combinations were studied. Of these, only 36 (26.5 percent) showed a statistically significant accumulation of metals in the tissue due to sediment exposure. In many of these cases, the demonstrated uptake was quantitatively marginal. Substantive uptake of some toxic metals occurred in some species; however, it was the exception rather than the rule.

4. There were important interspecific differences in the bioavailability of sediment-associated heavy metals. In most cases, a species accumulating a particular metal from one sediment did not accumulate the same metal from the other test sediments. This indicates that chemical and physical form, as well as the concentration of the metal in the sediment, determines the bioaccumulation of metals to the species in question. Results also indicate that the physical and chemical forms of a metal that are available for bioaccumulation are different for different species.

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5. The information and data published in this report are contributions to the further understanding of the complex nature of sediment, water, and chemical/biological interactions and establish a baseline from which to develop meaningful evaluations for the selection of an environmentally compatible disposal alternative. It is expected that the methodology employed in this study and the resulting interpretation of the chemical/ biological interactions will be of significant value to those persons concerned with CE dredged material permit programs.

John L. Cannon

JOHN L. CANNON
Colonel, Corps of Engineers
Commander and Director

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20. ABSTRACT (Continued).

Cont. → and Ashtabula, Ohio, harbor. The accumulation of eight heavy metals (cadmium, chromium, copper, iron, manganese, nickel, lead, and zinc) by all species and of two metals (mercury and vanadium) by selected species was measured.

Statistically significant accumulation of metals from sediment was demonstrated only 36 times (26.5%) out of 136 metal-species-sediment test combinations.

Variations in bioaccumulation were observed between species, metals, sediments, and salinity. In these studies, correlation was not observed between accumulation and specific metal forms as determined by selective chemical extraction of test sediments.

Bulk metal analyses of the test sediments also did not correlate with metal bioavailability.

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SUMMARY

Only a small percentage of the heavy metals that enter the aquatic environment remain in true solution. Most of the metals introduced become associated with clays, carbonates, organic matter, insoluble metal oxides and sulfides and other particulate material that form the sediments of the nation's waterways. When high amounts of these heavy metals enter the aquatic system from pollutional sources, the underlying sediments become enriched by several orders of magnitude over those from natural sources. On the other hand, the mobility and bioavailability become somewhat limited.

A considerable portion of these metal-enriched sediments find their way into the transportation waterways of this country. To maintain these waterways, the U.S. Army Corps of Engineers annually disposes of about 190,000,000 cubic meters (cu m) of dredged material in the nation's fresh and marine waters. The heavy metals contained in this dredged material could represent a potential hazard to aquatic ecosystems if the metals become available and are incorporated into aquatic organisms.

A review of the literature indicates that the knowledge of the availability to benthic organisms of metals contained in sediments is considerably restricted. There is some evidence both for and against correlation of metal concentrations in the sediments with concentrations in the associated benthic animals. In addition, little evidence was found to support the premise that bulk-sediment metal composition can be used to estimate the environmental impact of sediment-sorbed metals on the benthic

community. Instead, availability appears related to the chemical forms of the metals contained in the sediment and varies from one metal to another and between species of benthic organisms.

To provide additional information in this area, biological laboratory studies were conducted to determine the availability of sediment-adsorbed heavy metals to benthic invertebrates. For these studies, natural sediments from 3 different locations were selected to provide a range of chemical and physical properties along with elevated heavy metal levels. These sediments came from Texas City and Corpus Christi, Texas, Ship Channels and from Ashtabula, Ohio, Harbor. Five different test organisms (*Rangia cuneata*, *Palaemonetes pugio*, *Palaemonetes kadiakensis*, *Neanthes arenaceodentata*, and *Tubifex* sp.) were exposed to these sediments for periods up to 6 weeks to determine if the sediment-associated metals were available to the test animals. The accumulation of 8 heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) by all species and of 2 metals (Hg and V) by selected species was measured.

Twenty experimental exposures were performed over a 2-year period. Of the resulting 136 metal-species-sediment combinations, only 49 (36%) demonstrated a statistically significant relationship between exposure to sediment and heavy metal concentrations in the tissues of the experimental animals. In 13 of these cases, the effect of the sediment was inverse. That is, control animals contained significantly higher metal concentrations than did the sediment-exposed animals. Thus, a significant accumulation of a metal from sediment was demonstrated only 36 times (26.5%). In many cases where a statistically significant

accumulation of a metal from a sediment occurred, the uptake was quantitatively marginal and of doubtful ecological significance.

The results of this investigation indicate that it is extremely difficult to precisely assess the bioavailability of sediment-adsorbed heavy metals to benthic invertebrates. The relative availability of different heavy metals varies substantially and is influenced by the animal species used and the salinity at which exposure is performed. Replicate exposures performed under identical conditions yielded contradictory results, indicating the possibility of seasonal variations in the ability of animals to accumulate heavy metals from sediment.

In addition to the biological studies, various chemical extractants were evaluated to determine whether or not they could be used to predict or estimate the bioavailability of the sediment-sorbed metals. However, the small number of incidences of proven bioaccumulation found in this study made it impossible to correlate the phase in which the metals occurred in the sediment with their availability. Furthermore, no correlation existed between the bulk metal content of the test sediments and observed bioaccumulation.

The results of this study suggest that bioassays such as that recommended by the Environmental Protection Agency/Corps of Engineers Technical Committee on Criteria for Dredged and Fill Material may be the only way to determine bioavailability of metals in any given sediment containing high levels of metals. High metal levels alone do not indicate that substantial metal accumulation or adverse environment effects will occur.

In the evaluation of the bioavailability of heavy metals from dredged material, it is recommended that 2 or more species of different phylogenetic groups (eg. molluscs, annelid worms, shrimp) should be used and the exposures should be conducted at a salinity similar to that at the disposal site. Exposures of 3 to 4 weeks are deemed adequate.

PREFACE

This report is a summary of the work accomplished as a part of the Dredged Material Research Program (DMRP) Task 1D, "Effects of Dredging and Disposal on Aquatic Organisms," Work Unit 1D06, "Availability of Sediment-Adsorbed Heavy Metals to Benthos with Particular Emphasis on Deposit-Feeding Infauna." The study was conducted under Contract No. DACW 39-57-C-0096, dated 7 April 1975, between Texas A & M Research Foundation, College Station, Texas, and the U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Miss. The DMRP was sponsored by the Office, Chief of Engineers, U. S. Army, and monitored by the Environmental Laboratory (EL), WES.

The principal investigators were Dr. J. W. Neff, Associate Professor, Biology Department, and Dr. J. F. Slowey, Senior Research Chemist, Environmental Engineering Division, Texas A&M University. Dr. Jack Anderson, formerly Professor of Biology at Texas A&M and now at Batelle Northwest, also served as principal investigator during the early formative stages of the project. Mr. Robert Foster conducted the biological field sampling and laboratory studies under Dr. Neff's supervision. Drs. W. G. Weiss and John McHalfey assisted Dr. Slowey in the chemical analyses. The authors are especially indebted to Ms. Sherri Krezer, Melissa Morgan, and Becky Schult for their assistance in preparation of this report.

This study was conducted under the supervision of Dr. Richard K. Peddicord, Contract Manager, Environmental Impacts and Criteria

Development Project, EL, and under the general supervision of Dr. Robert M. Engler, Project Manager, EL, and Dr. John Harrison, Chief, EL.

Director of WES during the conduct of this study and the preparation and publication of this report was COL John L. Cannon, CE.

Technical Director was Mr. F. R. Brown.

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AVAILABILITY OF SEDIMENT-ADSORBED HEAVY
METALS TO BENTHOS WITH PARTICULAR
EMPHASIS ON DEPOSIT-FEEDING INFAUNA

PART I. INTRODUCTION

Background

1. Only a small percentage of the heavy metals that enter the aquatic environment remain in true solution. For the most part, they become or remain associated with insoluble metal oxides or sulfides, organic matter, carbonates, clays, and other particulate material. As a result, a large percent of the metals end up in the underlying sediments where metal concentrations may be several orders of magnitude higher than those in the waters. Natural background levels of most heavy metals in sediments are usually in the low milligrams/kilogram (mg/kg) range. However, man's impingement upon the aquatic environment has resulted in localized concentrations several orders of magnitude higher. This is especially true within portions of the waterways over which much of waterborne transportation occurs.

2. To maintain these waterways, the U.S. Army Corps of Engineers dispose of approximately 190 million cu m of dredged material in the nation's fresh and marine waters annually. Since this dredged material always contains a wide variety and range of heavy metals, both natural and man-induced, considerable concern exists over the potential, immediate and long-range, effects of these metals on aquatic and benthic organisms. Part of this concern stems from the uncertainties concerning whether metals present in these sediments are harmful

to the organisms or even if they are bioavailable. Whether justified or not, such concern has created problems for the Corps of Engineers in their disposal in open waters of this dredged material.

Scope of Study

3. The overall purpose of this study was to investigate the availability of selected sediment-sorbed heavy metals to benthic *deposit-feeding invertebrates*. It was also to develop, if possible, some method(s) of chemical extraction of sediments that might reflect the bioavailability of these metals.

4. To accomplish these objectives, the laboratory studies were divided into two phases. Phase I investigated methods for identifying the chemical and physical forms in which the metals were located within the test sediments. A total of 12 different chemical extractants or physical separations were evaluated and the results compared with those obtained using the Standard Elutriate Test (EPA 1975) and the selective sequential extraction method developed by the U. S. Army Engineer Waterways Experiment Station (WES) (Brannon, et al. 1976).

5. Phase II consisted of biological laboratory studies in which different benthic invertebrates were exposed to natural sediments of known heavy metal contamination. Specific objectives of these studies were

- a. To determine accumulation and uptake of the selected heavy metals by these test organisms;
- b. To determine the effect of salinity on heavy metal uptake;

- c. To investigate depuration of heavy metals after the test organisms are removed from the test sediments;
- d. To evaluate any correlation of tissue metal uptake with metals and metal forms present in the test sediments.

6. Metals investigated in this study were copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), mercury (Hg), nickel (Ni), chromium (Cr), manganese (Mn), and iron (Fe). Additional metals considered during parts of the study were arsenic (As), selenium (Se), cobalt (Co), vanadium (V), and antimony (Sb). Sediments used in the study included both marine sediments collected at several locations along the Texas coast and fresh water sediment from Ashtabula, Ohio. Test organisms consisted of both filter-feeding and deposit-feeding species and included a crustacean, an infaunal bivalve, and an infaunal polychaete for each test sediment.

PART II: LITERATURE REVIEW

Heavy Metal Concentrations in Benthic Invertebrates

7. It has long been recognized that freshwater and marine organisms contain in their tissues several heavy metals at concentrations many times higher than those in the ambient medium. This ability of aquatic organisms to concentrate potentially toxic heavy metals has led to concern about the impact of the ever-increasing influx of metals to aquatic ecosystems on public health aspects of our fishery resources. Because of these concerns, there is a large and rapidly growing amount of published literature dealing with the concentrations of different heavy metals in freshwater and marine animals. The earlier literature was reviewed by Vinogradov (1953) and Goldberg (1965). The more recent studies have been reviewed by Leland et al. (1975, 1976) and Leland and Luoma (1977).

8. High concentrations of heavy metals in the tissues of benthic invertebrates can often, but not always, be correlated to elevated levels of the metals in the adjacent water or sediments. Because of this, several investigators have recommended the use of benthic invertebrates, particularly bivalve molluscs, as indicators of local heavy metal pollution of the aquatic environment. This approach should be used with caution, since knowledge is incomplete about the bioavailability of different chemical species and different forms (soluble, food-adsorbed, or sediment-adsorbed) of the heavy metals to different species of benthic invertebrates.

9. Stenner and Nickless (1974) detected unusually high concentrations of Cd, Pb, and Zn in benthic organisms from a tributary of the Hardangerfjord in Norway. Oysters *Ostrea lutaria* from the Foveaux Strait, New Zealand, contained up to 9 grams/kilogram (g/kg) wet weight of Cd in their soft tissues (Nielsen 1975). Oysters *Crassostrea gigas* from the Derwent and Tamar estuaries in Tasmania contained similarly elevated concentrations of Cd, Zn, and Cu (Thrower and Eustace 1973). MacKay et al. (1975) showed that concentrations of Cd, Cu, Zn, Pb, and As in oysters *Crassostrea commercialis* increased from the mouth to the head of an estuary in New South Wales, Australia. Similarly, Cd concentrations in the tissues of the limpet *Patella vulgata* increased from the mouth to the upper reaches of the Bristol Channel, England (Shore et al. 1975). At Lodye Bay near the head of the Channel, the limpet tissues contained a mean of 537 mg/kg dry weight of Cd. The concentrations of Cd, Cu, and Zn in oysters *Crassostrea virginica* from Chesapeake Bay were found to increase toward the mouth of the estuary (Huggett et al. 1973). Topping (1973) determined the concentrations of Cd, Cu, Pb, and Zn in the tissues of marine molluscs and crustaceans from Scottish coastal waters. With the exception of copper, tissue heavy metal levels were not related to known levels of pollution. Highest tissue Cd concentrations were found in animals from the Orkney and Shetland Islands, areas considered relatively unpolluted. Fowler et al. (1975) measured the concentrations of several heavy metals in the tissues of dover sole, *Microstomus pacificus*, and crabs *Cancer anthonyi* and *Mursia gaudichaudii* from southern California

coastal waters. Metal concentrations in animals from a "contaminated" area (Point Vicente, Palos Verdes) and an "uncontaminated" area off Santa Barbara were compared. With two exceptions, there was no clear relationship between the collection site and tissue levels of 18 metals. The exceptions were arsenic and selenium concentrations. Tissue arsenic concentrations were significantly higher in fish from the contaminated area (4.12 mg/kg) than from the uncontaminated area (2.43 mg/kg). Fish tissue selenium concentrations were not significantly different in the two populations. The crabs *C. anthonyi* had much higher tissue arsenic concentrations and individuals from the uncontaminated area had significantly higher levels (51.02 mg/kg) than those from the contaminated area (17.29 mg/kg). Selenium showed the same trend, with mean crab tissue concentrations of 15.66 mg/kg and 5.14 mg/kg in individuals from the uncontaminated and contaminated areas, respectively. Penrose et al. (1975) determined the distribution of arsenic in seawater, sediments, and selected biota of Moreton's Harbour, Newfoundland, which had received arsenic-bearing drainage from a stibnite mine for more than 38 years. Arsenic concentrations in the surface water declined to normal within 200 meters (m), and in sediments within 50 m of the outfall. Animals did not show significantly higher tissue As levels near the mine, with the exception of the sea urchin, *Strongylocentrotus droebrachiensis*, which contained significantly higher concentrations of As (80 mg/kg) near the mine than at control stations (5.4 mg/kg). Trace metal concentrations in mussels, *Mytilus californianus*, from the

southern California coast were related to pollutant sources (Alexander and Young 1976). Tissue levels of Pb were correlated with diffuse inputs, while those of Cu, Cr, and Ag were closely correlated to inputs from urban point sources.

10. Chow et al. (1976) measured the concentrations of Pb in marine plants and animals from the coastal regions of southern California. For the molluscs and crustaceans studied, tissue Pb concentrations reflected the chemical environment of their habitat. Invertebrates with high Pb concentrations were found in industrialized coastal regions. For example, Pb concentrations in tunicates *Styella montereyensis* increased from 1.27 mg/kg at Rincon Point and Gaviota to 2.86 mg/kg at San Diego and 14.5 mg/kg at Long Beach. Cockles *Protothaca staminea* showed a similar trend with mean tissue Pb burdens of 0.41 mg/kg at Rincon Point to 5.56 mg/kg at Anaheim Bay near a gasoline fueling dock. Habitat also had an effect on Pb concentrations. Abalone (several species of *Haliotis*) from a subtidal rocky substratum had mean Pb levels of 0.05 mg/kg. Limpets *Lottia gigantea* and turbins *Tegula funebris* from the upper intertidal zone had mean tissue Pb concentrations of 0.84 mg/kg and 0.59 mg/kg, respectively. Horowitz and Presley (1977) reported that Pb concentrations in zooplankton collected from the South Texas outer continental shelf (Port Aransas to Brownsville, Texas) increased from north to south. Concentrations of Cd increased from nearshore to offshore, mirroring the concentrations of Pb and Cd in the bottom sediments.

11. Enk and Mathis (1977) studied the distribution of Cd and Pb

in different components of a relatively unpolluted Illinois stream ecosystem. Both metals were detected in all components investigated. Cadmium concentrations were similar in the fish and sediments, while aquatic insects contained higher Cd concentrations than the sediments. Lead concentrations were similar in sediments and aquatic insects and higher than in fish. Snails had the highest levels of Pb. In general, the concentrations of both metals increased successively from water to fish to sediments to aquatic insects. Thus, there was no indication of food chain magnification of Pb and Cd in this ecosystem. Ireland and Wootton (1977) studied the distribution of Pb, Zn, Cu, and Mn in the marine gastropods *Thais lapillus* and *Littorina littorea* collected during the same month from nine coastal stations in Wales. The concentrations of Pb, Zn, and Cu in the whole bodies of *Thais* were higher than those in *Littorina* at all stations. The metal concentrations in the two species did not vary in parallel at different stations. The two species at a particular site behaved as though they were experiencing different environmental levels of the metals, probably reflecting differences in their mode of life.

12. Boyden (1974) examined the relationship between body weight and tissue heavy metal content in six species of estuarine molluscs. Concentrations of heavy metals tended to increase with increasing body weight in all species examined, but the mathematical relationship between body weight and metal content varied for different metals and different species. On the other hand, Anderlini (1974) could find no correlation between body weight of the red abalone (*Haliotis rufescens*)

from five locations along the California coast and tissue levels of eight heavy metals. Martin (1974) determined the concentrations of several metals in the crab *Cancer irroratus* in relation to several physical and biological parameters. Of the metals studied, only the concentration of Mn was positively correlated with body size. Concentrations of other metals were not related to body weight. However, there was a close, positive correlation between the concentrations of Cu and Zn in the crab tissues. MacKay et al. (1975) found an inverse relationship between the tissue concentration of five heavy metals and the age and weight of oysters *Crassostrea commercialis* from New South Wales.

13. Several investigators have observed seasonal variations in the concentration of heavy metals in benthic invertebrates. Fowler and Oregoni (1976) measured the concentration of 10 heavy metals in tissues of mussels *Mytilus galloprovincialis* at different seasons and from 15 stations along the coast of the northwest Mediterranean Sea. Seasonal variations in metal concentrations were most marked in mussels collected near ports and at the mouth of the Rhone River (Port St. Louis). Largest average seasonal fluctuations were observed for Cr, Cd, and Pb with seasonal maxima occurring in March, a time of high rainfall and runoff from land. They attempted to correlate metal concentrations in mussels with those found in ambient waters. Copper and zinc maxima in both mussels and water occurred simultaneously at several stations. Maximum levels of Cd in mussels and water coincided in March but there

was no correlation between maxima in June or December. Ireland (1974) studied seasonal variations in the concentrations of Zn, Cu, Mn, and Pb in barnacles *Balanus balanoides* from Cardigan Bay, Wales. High tissue concentrations of Zn and Cu were found in November and March, while the highest concentration of Mn was found in samples collected in June. No seasonal variations in Pb concentrations were observed. The lowest concentrations of Zn and Cu were found during the summer months possibly due to either a decreased rate of river flow or an increased phytoplankton productivity during this season. Scallops *Pecten maximus* and *Chlamys opercularis* were collected from the same area of the English Channel at different seasons and analyzed for 11 heavy metals (Bryan 1973). Mean tissue concentrations of Ag, Co, Cr, Cu, Mn, Ni, Pb, and Zn were higher in *Chlamys* than in *Pecten*, but the reverse was true for Al, Cd, and Fe. In both species, seasonal changes in the concentrations of Co, Cu, Fe, Mn, Ni, Pb, and Zn were observed with the highest levels generally occurring during the autumn and winter months. The seasonal changes seemed to be inversely correlated to food supply, since tissue metals concentrations were usually highest when phytoplankton productivity was low and tended to fall when phytoplankton productivity increased in the spring. Galtsoff (1964) observed elevated levels of Mn, Fe, Cu, and Zn in the soft tissues of oysters *Crassostrea virginica* in the summer followed by depressed levels in the winter. Seasonal dynamics of Mn, Fe, Zn, Cu, and Cd were investigated in a genetically similar population of oysters *Crassostrea virginica* in the Rhode River, a tributary of Chesapeake Bay (Frazier 1975). Annual cycles resulting

in the turnover of large portions of the body burden were observed for all metals studied. Two patterns of metals dynamics were described. Concentrations of Mn and Fe in soft tissues were significantly correlated with periods of shell deposition. A Mn turnover rate in the soft tissues of approximately two times the body burden per day occurred during the shell deposition period. Tissue concentrations of Zn, Cu, and Cd exhibited a gradual increase during the spring and early summer followed by a rapid loss during the late summer and early fall. During this latter period, 33% of the Zn and 50% of the Cu was lost in 4 weeks. There was also a 50% reduction in tissue Cd within 11 weeks. Tissue levels of these three metals seemed to be related to seasonal reproductive cycles in the oysters.

14. Several investigators have observed that trace metal concentrations in skeletal structures of benthic invertebrates are sometimes quite different from those in the soft tissues. Bertine and Goldberg (1972) determined the concentrations of Rb, Fe, Co, Sb, Sc, Ag, Cr, Zn, Se, and Hg by neutron activation analysis in the shells of clams, mussels, and shrimp. Shells of clams (several species of *Ensis*) with aragonitic shells and of mussels (several species of *Mytilus*) with mixed aragonitic and low-Mg calcite shells, both freshly caught and museum specimens up to 100 years old, were analyzed in an effort to determine if trace element content might be related to anthropogenic changes in the composition of inshore marine waters. No temporal pattern of change was observed. The aragonitic and combined calcitic-aragonitic shells had similar trace metal compositions suggesting that

the chemical composition of the water in which they grew was the primary determinant of their trace element composition. The proteinaceous molts of the shrimp contained high concentrations of the metals studied. The authors suggested that sequestration of metals in skeletal structures might be a means by which the animals remove unwanted and potentially toxic metals from their soft tissues. In support of this hypothesis, Wright (1976) observed that the Cd concentration (a nonessential element) was higher in the exoskeleton than in other tissues of the crab *Carcinus maenus*, whereas Zn and Cu concentrations (both essential micronutrients) were not as high in the exoskeleton as in several other tissues. Chow et al. (1976) showed that the Pb content (nonessential) of the carapace of the crustaceans, *Panulirus interruptus*, *Cancer sp.*, and *Cancer antennarius*, was significantly higher than that of the dry tissues. Horowitz and Presley (1977) reported that exoskeletons of shrimp and the skin of both squid and fish generally contained higher concentrations of several heavy metals than did the flesh of the same organisms. Squid pens contained elevated levels of Cu, Cd, Zn, Pb, and Fe in comparison to the skin and flesh. They suggested that these elevated metals levels in skin and skeletal structures might represent an internal detoxification procedure and/or a means of storing essential micronutrients such as Cu, Mn, and Fe. Sturesson and Reymont (1971) studied the effect of salinity on the concentrations of Cr, Mg, Zn, and Cu in the aragonitic shells of the mollusc *Macoma balthica* from the Baltic Sea. Shells from low salinity water had higher concentrations of Cr. Those from the more saline regions of the Baltic had higher

concentrations of Mg and Cu. The Zn concentration of the shells did not vary with salinity. The concentrations of Pb, Hg, Cd, Zn, Cu, and Cr in shells of oysters *Crassostrea virginica* from several Atlantic Gulf coast stations were measured (Ferrell et al. 1973). All metals studied were present at concentrations many orders of magnitude higher than those in seawater. Little or no geographic variation was noted. Particularly high concentrations of Pb (38-41 mg/kg) and Cu (43-70 mg/kg) were found. Stuesson (1976) examined incorporation of Pb from seawater into the shell of *Mytilus edulis*. Highest Pb incorporation occurred in the calcium carbonate deposited during the exposure period and in the older parts of the periostracum.

15. A complicating factor in the interpretation of data on the heavy metals concentrations in the tissues of benthic invertebrates is the fact that several of these metals are known to be essential micronutrients for animals. Included in this category are Fe, Mn, Cu, Zn, Co, V, Cr, and Se. Because of these requirements, aquatic organisms have evolved mechanisms for accumulating them from dilute solution in the ambient medium. These uptake mechanisms may account for the rapid accumulation and high toxicity of these metals when they are present in solution at concentrations only slightly higher than normal. Zinc is part of the prosthetic group of several enzymes. However, its concentration in the tissues of oysters *Ostrea edulis* is far in excess of the amount present in the zinc-dependent enzymes (Coombs 1972). The requirements for copper vary from species to species. In those species of molluscs and arthropods which possess the copper-containing respira-

tory pigment, hemocyanin, tissue, and plasma, copper concentrations are maintained at a high level compared to that of the ambient medium. For instance, concentration factors (concentration in tissues/concentration in water) for copper of 2.1×10^6 and 4.2×10^4 have been reported for the squid *Loligo opalescens* (Martin and Flegal 1975) and the crab *Cancer irroratus* (Martin 1974), respectively. Bryan (1968) found that marine decapod crustaceans tend to regulate serum and tissue copper concentrations in the range of 20-35 $\mu\text{g/g}$. Marine animals which lack hemocyanin generally have lower copper concentrations (Topping 1973; Windom et al. 1973; Cross et al. 1973).

Accumulation of Heavy Metals from Food and Water

16. As indicated in the previous section, the concentrations of heavy metals in the tissues of benthic invertebrates are usually higher than those in the surrounding environment, indicating a net accumulation of these materials from environmental sources. There are three possible sources of heavy metals to benthic invertebrates. These are metals in solution or colloidal suspension in the water, metals in food or ingested particulate materials, and metals present in different forms in bottom sediments. There has been considerable controversy in recent years among ecologists and environmentalists concerning the relative importance of these three potential sources in the contamination of benthic animals with heavy metals. The question is proving very difficult to resolve since animals in nature are nearly always exposed to the metals in all three forms. Even in carefully

controlled laboratory studies, there is often an element of uncertainty as to whether metals introduced in one form might be transformed to another form before absorption by the animal.

17. There is a very large body of published information concerning the accumulation of heavy metals from aqueous solution by benthic invertebrates. The potential of a metal for bioaccumulation is often measured as the concentration factor (the ratio of the concentration of the element in the organism to that in the ambient water). Waldichuk (1974) lists concentration factors for 20 metals in marine phytoplankton, zooplankton, macroinvertebrates, and fish. In nearly all cases, the concentration factors were higher for the macroinvertebrates than for other organisms. Concentration factors in the macroinvertebrates were highest for Zn (148,000-290,000), Cd (82,000-182,000), Cu (24,000-35,000), Pb (7,000-100,000), and As (300-3,300). Although it is usually assumed that concentration factors are equilibrium ratios, care should be taken in interpreting and comparing these numbers, since such factors as duration of exposure, exposure concentration, temperature, salinity, etc. may have a large effect on the values obtained. Concentration factors for *Mytilus edulis* exposed to Pb for 130 days in the laboratory were approximately 26,000, 31,000, and 8,000 at exposure concentrations of 0.5 mg/l, 1.0 mg/l, and 5.0 mg/l Pb, respectively (Schulz-Baldes 1972). Mussels exposed in the field to natural Pb levels of 0.2 µg/l had a concentration factor of 42,000. Concentration factors for inorganic As in crayfish *Procambarus clarkii* exposed for 18 days to 0.01 mg/l, 0.10 mg/l, and 1.0 mg/l As were 480, 95, and 90, respectively (Woolson et al. 1976).

For oysters, *Crassostrea virginica*, exposed to mercuric acetate for 45 days, concentration factors were 1210 and 916 at exposure concentrations of 10 µg/l and 100 µg/l Hg, respectively (Cunningham and Tripp 1975). Mercury concentration factors of 1230, 923, 455, and 441 were reported for oysters following exposure for 256 hours to 10, 40, 80, and 100 µg/l respectively, of Hg as mercuric chloride (Mason et al. 1976).

18. Zitko and Carson (1975) studied the accumulation of thallium from seawater by clams *Mya arenaria* and mussels *Mytilus edulis*. The clams accumulated more Tl than did the mussels. Concentration factors in the range 11 to 19 were lower than for most other metals. Unlu et al. (1972) studied the accumulation of $^{203}\text{HgCl}$ by the mollusc *Tapes decussatus*. Uptake was rapid with highest Hg levels occurring in the viscera and gills. Molluscs exposed to Hg-contaminated phytoplankton lost Hg more rapidly than those exposed to Hg in solution when the two groups of molluscs were returned to Hg-free seawater. Oysters, *Crassostrea virginica*; scallops, *Aquiducten irradians*; and lobsters, *Homarus americanus*, exposed for 21 days to 10 µg/l soluble Cd as $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, accumulated 1.49 mg/kg, 2.46 mg/kg, and 0.72 mg/kg Cd (wet weight), respectively, in their tissues (Eisler et al. 1972). These values were all higher than those in the corresponding control animals indicating uptake even at this very low exposure concentration. Similarly, Gillespie et al. (1977) reported that the crayfish, *Oreoneustes propinquus propinquus*, accumulated a mean concentration of 18.4 mg/kg during 190.5 hours exposure to 10 µg/l Cd as $\text{Cd}(\text{Cl}_2)$. Timourian

and Watchmaker (1972) demonstrated a rapid accumulation from solution of ^{63}Ni by embryos of the sea urchin *Lytechinus pictus*. Little Ni uptake occurred before fertilization but was rapid immediately after, reaching equilibrium in 20-30 minutes. Pentreath (1973) studied the accumulation from water of ^{65}Zn , ^{54}Mn , ^{58}Co , and ^{59}Fe by the mussel, *Mytilus edulis*. Greatest accumulation of all four radionuclides occurred in the stomach and digestive gland. Little difference was found in the uptake of soluble and particulate forms. It was suggested that both forms could be bound by the mucus sheets used in feeding.

19. Oysters *Crassostrea virginica* accumulated 40 mg/kg, 33 mg/kg, and 23 mg/kg Hg in their tissues during 10 days exposure to 50 $\mu\text{g/l}$ Hg as mercuric chloride, methylmercuric chloride, and phenylmercuric chloride, respectively (Kopfler 1974). However, after 74 days exposure to 1 $\mu\text{g/l}$ concentrations of the three mercury salts, methyl- and phenylmercury were concentrated to the same degree (40 mg/kg), while inorganic mercury was accumulated to about one-fourth this concentration.

Freshwater clams *Anodonta grandis* were exposed to 1 to 100 $\mu\text{g/l}$ Hg as mercuric chloride, methylmercuric chloride, and phenylmercuric chloride for 3 weeks (Smith et al. 1975). The clams concentrated the metal in the order methylmercuric chloride > phenylmercuric chloride > mercuric chloride. The rate of uptake increased with increasing Hg concentration in the eater. Temperature had no significant effect on uptake rates or on elimination. Beque et al. (1971) studied the accumulation of different chemical forms of ruthenium by the freshwater snail *Lymnaea stagnalis*. After 5 days exposure, concentration factors

for Ru were highest for animals exposed to RuCl_3 , intermediate for $\text{RuNO}(\text{NO}_3)_3$ and $\text{RuNO}(\text{OH})_3$, and low for RuNOCl_3 and $\text{Na}_2[\text{RuNO}(\text{NO}_2)_4(\text{OH})]$. For RuCl_3 and $\text{RuNO}(\text{NO}_3)_3$, the uptake was more rapid at a temperature of 15°C than at either 5° or 25°C . The scleractinian coral *Pocillopora verrucosa* accumulated arsenate from solution but converted most of it rapidly to arsenite which was lost back to the water (Pilson 1974). Freshwater snails *Helisoma companulata* rapidly accumulated phenylmercuric acetate from solution. The absorbed phenylmercuric acetate was converted mainly to inorganic mercury which was eliminated from the tissues very slowly (Fang 1973).

20. Kinkade and Erdman (1975) studied the effect of water hardness on the accumulation of Cd by fresh water snails *Ampullaria paludosa*. The initial Cd uptake rate was higher in hard water than in soft water. However, the total amount of Cd accumulated was greater in snails in soft water than in those in hard water. Hutcheson (1974) showed that the rate of accumulation of Cd by the blue crab *Callinectes sapidus* was higher at low salinities and high temperatures. Bryan (1974) compared the uptake of heavy metals from solution by worms *Nereis diversicolor* collected from metals-contaminated sediments and from uncontaminated sediments. Earlier studies had shown that the former worms were highly tolerant to the high levels of heavy metals characteristic of their habitat. Copper-tolerant worms accumulated Cu more rapidly than nontolerant worms. Zinc-tolerant worms were less permeable to Zn and excreted it more rapidly than nontolerant worms.

Worms from Cd-rich sediments absorbed Cd approximately 15% more slowly than nonadapted worms. Worms living in sediments containing 500 mg/kg As absorbed aqueous ^{74}As more rapidly and to a greater degree than worms from low-As environments. Rates of Pb uptake and loss by large mussels *Mytilus edulis* were less than those by small mussels (Schulz-Blades 1974). Similarly, small oysters *Crassostrea virginica* accumulated more Hg/g wet weight than did large oysters (Cunningham and Tripp 1975).

21. Seasonal dynamics of heavy metals in oysters, *Crassostrea virginica* place at relatively uncontaminated and heavily contaminated stations in the Rhode River, Maryland, were investigated (Frazier 1976). Oysters from both control and contaminated stations showed wide seasonal fluctuations in tissue burdens of several metals, particularly Cd, Mn, and Fe. Generally, metals levels in oysters from the contaminated area were higher than those in oysters from the control station. The enhancement of metals in the soft tissues of oysters exposed to the contaminated environmental conditions relative to the controls reflected the pattern of metal contamination of the sediments. Uptake of metals by the oysters was seasonally dependent with rapid uptake occurring in the summer and fall and depressed uptake occurring in the early spring. Zarogian and Cheer (1976) exposed oysters *Crassostrea virginica* to 5 $\mu\text{g/l}$ Cd as $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ for 40 weeks. During this time, the oysters accumulated up to 10.75 mg/kg Cd in their tissues. The rate of Cd accumulation in the summer was more than twice that in the winter and spring. Jackim et al. (1977) reported that temperature, salinity,

bottom sediment type, and Zn concentration all influenced the uptake of Cd by four species of marine bivalve molluscs, *Mytilus edulis*, *Mulinia lateralis*, *Mya arenaria*, and *Nucula proxima*. There were wide interspecies variations in Cd uptake patterns. *Mytilus* consistently accumulated Cd several times more rapidly than did *Mya*. An increase in temperature or a decrease in salinity increased Cd uptake by all four species. *Mya* accumulated the greatest amount of Cd when held without substrate and progressively less when held in sand or mud sediments. Zinc at concentrations of 0.5 ppm substantially decreased Cd uptake by *Mytilus* and *Mulinia*. Phillips (1976, 1977) studied the effects of different constant salinities and temperatures and of salinity fluctuations on the uptake of Zn, Cd, and Cu by the mussel *Mytilus edulis*. No effect of constant temperatures (10-18°C) or salinities (15-35‰) on Zn uptake were observed. However, Cd and Cu uptake were greater at the lower salinity. Despite the well established effects of decreased salinity on filtration rate and oxygen consumption of mussels (Bayne 1976), the net uptake of Zn by mussels exposed to four fluctuating salinity regimes for 5 days did not differ significantly. The net uptake of Cd and Cu was greater in mussels from the lower final salinity. However, when mussels were subject to a highly stressful rapid salinity increase, net Zn uptake was significantly increased.

22. The role of food as a source of heavy metals to benthic invertebrates has also been investigated. Renfro et al. (1975) studied the uptake of ⁶⁵Zn from seawater or from combined seawater and food by

shrimp, *Lysmata seticaudata*, and crabs, *Carcinus maenas*. Contaminated food consisted of ^{65}Zn -labelled *Artemia* and mussels *Mytilus galloprovincialis*. Shrimp and crabs receiving ^{65}Zn from food and water did not attain significantly higher ^{65}Zn body burdens than those individuals that accumulated the isotope from the water only, suggesting a low bioavailability of food-adsorbed Zn to these species. Young (1975) studied the transfer of ^{65}Zn and ^{59}Fe from the marine alga *Fucus serratus* to the snail *Littorina obtusata*. Snails feeding on the labelled algae accumulated ^{65}Zn and ^{59}Fe in their tissues. Based on calculations of Zn and Fe accumulation from food and seawater, food was found to be the more important source of these metals to the snail. Rates of Pb uptake from sea water and food were similar for the mussel *Mytilus edulis* (Schulz-Baldes 1974). Mussels fed algae *Dunaliella marina* containing Pb, accumulated approximately 23.5% of the Pb available in 35 days. Those exposed to Pb in solution accumulated approximately 29% of that available. The Pb quantity given per mussel per day was about 2 μg in both test series. An aquaculture system containing algae, oysters, and clams was dosed continuously with Cd (6-100 $\mu\text{g}/\text{l}$). Accumulation of Cd by the molluscs was linear with time for more than one month (Kerfoot and Jacobs 1974). Cadmium accumulation was primarily by uptake from solution, although the oysters and clams did accumulate a small amount of Cd from ingestion of the algae. Oysters *Crassostrea gigas* were shown to accumulate ^{60}Co primarily from ingestion of suspended particulate matter, whereas ^{137}Cs was accumulated primarily from solution (Harrison et al. 1976).

Accumulation of Heavy Metals from Sediments

23. It has been suggested that sediment-bound heavy metals may be an important source of heavy metals for benthic infaunal and deposit-feeding invertebrates (Lowman et al. 1971; Wolfe and Rice 1972; Schubel 1972). However, there is very little unequivocal evidence of the direct accumulation and assimilation of sediment-bound heavy metals by benthic invertebrates. For a number of reasons, this evidence has proven difficult to obtain. One of the problems has been that it is usually difficult or impossible to expose animals to sediment-adsorbed and particulate metals alone. As indicated in the previous section, accumulation from solution is rapid for most metals. The presence of even low concentrations of solute metal will significantly contribute to metals uptake by the animals and will confuse attempts to quantitate accumulation from sediments. This problem is particularly important in laboratory exposures in which the sediments are artificially metal-loaded, since chemical speciation and equilibration may allow for significant backflux of metals from the solids to the solute phase. In field studies, a correlation between metals concentrations in the sediments and those in the associated biota may indicate transfer of metals from the sediment to the animals or may merely be indicative of a common source of the metals to the sediments and biota. A second problem is related to the fact that deposit-feeding and particulate-feeding benthic invertebrates may contain significant amounts of unassimilated sediment-adsorbed heavy metals in their digestive tracts.

Whole-body analyses of these animals may greatly overestimate metal accumulation by the tissues of these animals. Even when these considerations are taken into account the results are not always conclusive. As pointed out by Elwood et al. (1976), for some elements more than 90% of the body burden of some test organisms could be associated with gut contents and surface contaminants. It is often difficult to know from the literature if whole body burden metal levels are for gut-purged or unpurged animals so that what might be reported as uptake may not be.

24. Cross et al. (1970) studied the relationship between trace metals concentrations of sediments in a coastal plain estuary and the concentrations of metals in six species of polychaetes occupying these sediments. The concentrations of Zn, Mn, and Fe in the worms from different sediments varied little, indicating either that these metals were regulated by the worms or that they were in a chemical form in the sediments not available to the worms. Bryan (1971) reported similar observations for the polychaete *Nereis diversicolor*. Ayling (1974) studied the concentrations of Cd, Zn, Cu, Pb, and Cr in oysters *Crassostrea gigas* from 15 sampling stations along the Tamar River estuary, Tasmania. Concentrations of Cd, Zn, and Cu in the oysters were consistently 10-40 times the concentrations in the inhabited sediments. Based on the assumption that the sediments were the source of the heavy metals in the oysters, Ayling defined three patterns of accumulation. Maximum Cu and Cr tissue concentrations were directly correlated with size of the oysters and were independent of the concen-

trations of these metals in the sediment. Lead was only absorbed where sediments contained a high concentration of this metal. Tissue concentrations of Zn and Cd were directly correlated with the concentrations of these metals in the sediments at the collection site. However, Ayling did not prove that the metals were not accumulated from the overlying water. Bryan and Hummerstone (1971) demonstrated that the Cu and Cd concentrations in the polychaete *Nereis diversicolor* from different locations were roughly proportional to the concentrations of Cu and Cd in the inhabited sediments. However, the concentrations of Zn, Pb, Mn, and Fe in the worms were not correlated to the concentrations of these metals in the sediments. For Zn in particular, the levels in the worms were remarkably constant over a wide range of sediment Zn values. Mathis and Cummings (1971) determined the concentrations of several metals in clams, tubificid annelids, and sediments from the Illinois River. They found that the concentrations of Cu, Ni, Pb, Cr, Zn, Co, and Cd in both the clams and worms were closely correlated to the levels of these metals in the associated sediments. Drifmeyer and Odum (1975) reported significantly higher lead concentrations in the grass shrimp, *Palaemonetes pugio*, collected from ponds inside diked dredged material disposal areas where the tissue lead concentrations averaged 11 ± 1.8 mg/kg as compared to shrimp from natural marsh areas where the tissue lead concentration was 0.2 ± 0.3 mg/kg. They suggested that the shrimp's method of food collection, namely ingesting sediment and particulate matter, apparently accounted for the increased Pb content of the dredged material area shrimp. Similar

results were observed for Mn. Valiela et al. (1974) applied metal-containing sewage sludge and urea fertilizers to salt marsh plots in southeastern Massachusetts and monitored heavy metals concentrations in the marsh and in the molluscs, *Mercenaria mercenaria*, *Crassostrea virginica*, and *Modiolus demissus*, in the tidal creeks of the marsh. All three species of shellfish showed no increase in tissue Pb or Zn concentration, but all showed elevated Cd related to the sludge-fertilizer application.

25. The mussel *Mytilus edulis* accumulated particulate ferric hydroxide to high concentrations (George et al. 1976). Accumulation was in linear proportion to the seawater concentration and occurred in all tissues examined. Particulate Fe was taken up by pinocytosis by specialized epithelial cells in the gill, gut, and kidney and held in intracellular membrane-bound vesicles. There was no free Fe in the cytoplasm of the cells. Approximately 30% of the Fe in the gut was unabsorbed and was rapidly excreted in the feces. A major portion of the absorbed Fe was excreted by transfer to the byssal threads. Dean (1974) could not demonstrate accumulation by tubificid worms of ^{65}Zn , ^{54}Mn , ^{60}Co , ^{59}Fe , or ^{51}Cr from Columbia River sediments. Renfro and Benayoun (1974) showed that the polychaete *Nereis diversicolor* accumulated ^{65}Zn in its tissues from organic particulate-bound ^{65}Zn on the surface of marine sediments and from iron-oxide bound ^{65}Zn on the surface of the same sediments. Rates of uptake from the two sources were similar. Long-term experiments on the uptake of ^{65}Zn from sediments by the polychaete *Hermione hystrix* showed that 60 or more

days of exposure to the sediments were required for the worm to approach a steady state with ^{65}Zn in the sediment (Renfro 1973). Amiard-Triquet (1975) compared the accumulation of ^{60}Co and ^{137}Cs from the water and from sediments by four deposit-feeding benthic species: the polychaete *Arenicola marina*; the heart urchin *Echinocardium cordatum*; and two lamellibranch molluscs *Scrobicularia plana* and *Macoma balthica*. For both metals and all species, accumulation was more rapid from solution than from sediments. The author concluded that the main vector of Co and Cs contamination of benthic marine invertebrates was water. However, these infaunal invertebrates did contribute significantly to the redistribution within the sediments, of radioelements absorbed on the surface. Renfro (1973) found that polychaete worms *Nereis diversicolor* burrowing through a sediment artificially spiked with ^{65}Zn , caused ^{65}Zn losses from the sediment to the water 3-7 times higher than from sediments without worms. Ueda et al. (1976) compared ^{115}Cd accumulation from sediments and seawater by the polychaete worm *Nereis japonica*. To accomplish this, one group of worms was allowed to come in contact with ^{115}Cd -spiked sediment during the exposure period. For the second group, a Saran net placed over the surface of the sediment prevented the worms from coming in direct contact with the sediment. Radionuclide levels in the overlying water were shown to be similar in the two exposure regimes. After 8 days exposure, worms in direct contact with ^{115}Cd -spiked sediments had accumulated six times more ^{115}Cd than had worms that were not in contact with the sediment. However, considering the

relative concentrations of ^{115}Cd in the sediments and overlying seawater, uptake from water was calculated to be 200 times more efficient than from sediments. Ueda et al. (1977) recently extended these experiments to estimates of bioavailability of several other sediment-adsorbed heavy metal radioisotopes. They calculated that uptake from water by the polychaete *Nereis japonica* was 120, 440, 1000, and 30 times more efficient than from sediments for ^{60}Co , ^{95}Zr , ^{95}Nb , ^{106}Ru , ^{106}Rb , and ^{137}Cs , respectively. Luoma and Jenne (1975a) conducted similar experiments with the deposit-feeding estuarine clam *Macoma balthica* and ^{109}Cd . Several types of sediment- ^{109}Cd complexes were compared. One group of clams was allowed to feed directly on the ^{109}Cd -laden sediments and a second group was placed in dialysis bags and then placed in the sediments, thus preventing direct contact between the clam and sediments but allowing access to solute-phase ^{109}Cd . Differences in ^{109}Cd accumulation were recorded as uptake directly from the sediment. Bioavailability of organically bound ^{109}Cd to the clams was very low. Ingestion of ^{109}Cd -laden iron oxide, however, resulted in significant uptake by the clams. If the $^{109}\text{CdFe}_x\text{O}_y$ developed an organic coating, availability declined significantly. A similar pattern was demonstrated for the polychaete *Nereis succinea* and the shrimp *Palaemon dibilis* (Luoma 1974). Accumulation of Hg bound to organic sediment was less than accumulation of Hg complexed to iron oxide sediments. Luoma and Jenne (1975b) also studied the availability of sediment-bound radioisotopes of Co, Ag, and Zn to *Macoma balthica*. Little Zn or Co uptake could be demonstrated when those metals were coprecipitated with amor-

phic iron oxide or manganese oxide. However, Ag was accumulated by the clam from the iron oxide precipitate and all three metals were accumulated from detrital organics. Accumulation rates of Co, Zn, and Ag were higher when these metals were adsorbed to biogenic carbonates (powdered mollusc shells) than when they were adsorbed to other substrates. Sinks from which bioaccumulation of bound metals was greatest also showed the greatest rate of sediment to water desorption of the metals. Beasley and Fowler (1976) exposed the polychaete worm *Nereis diversicolor* to marine sediments which had been contaminated with plutonium and americium either through the testing of nuclear devices or by the release of liquid waste effluent from a nuclear fuel reprocessing plant. Less than 0.5% of the sediment concentrations of these metals was accumulated by the worms. Pu uptake from both types of sediment was comparable. However, relatively more Am was accumulated from the waste effluent-contaminated sediment than from the nuclear test debris sediments. They concluded that water might be the predominant pathway for Pu accumulation by deposit feeding infauna.

Characterizations of Metals in Sediments

26. Lack of information on the physical and chemical forms of metals within sediments has created some of the uncertainty about the bioavailability of these metals. Metals in sediments can occur in many different chemical and physical forms. Among these are (1) water soluble in interstitial solution -- both complexed and ionic, (2) on

normal exchange sites, (3) on specific sorption sites, (4) occluded with hydrous oxides, (5) in organic matter, (6) as sulfides, and (7) in the lattice structure of minerals. Until recently, few attempts have been made to determine the amounts of various metals present in these fractions in fresh water or marine sediments. However, soil chemists in their attempts to determine "availability" of metals to plants have been studying such fractionation in soils for some time and have developed a number of analytical schemes for this purpose as well as for estimation of metal forms in soils (Black 1965; Holmgren 1967; Smith and Shoukey 1968; Lindsay and Norvell 1969; Patrick and Turner 1968; Gotoh and Patrick 1972, 1974; McLaren and Crawford 1973).

27. As early as 1958, similar techniques were applied to sediments when Goldberg and Arrhenius used ethylenediaminetetraacetic acid (EDTA) to remove "soluble" metals from sediments and Hirst and Nichols used acetic acid to extract "non-detrital" sediment metals. Lenhard et al. (1962) used modified soil extraction techniques to attempt classification of sediments in the Apies River. Hydroxylamine hydrochloride and acetic acid were used by Chester and Hughes (1967, 1969) to differentiate between land or "lithogeneous" and marine or "hydrogeneous" derived metals in Pacific Ocean sediments. Presley et al. (1972) sequentially extracted British Columbia fjord sediments with acetic acid-hydroxylamine hydrochloride ("reducible" phase), hydrogen peroxide ("oxidizable" phase), and hydrofluoric-nitric-perchloric acids ("residual" phase). They reported that the "reducible" phase included

metals associated with carbonates, hydrous oxides, and some sulfides. The "oxidizable" phase represented metals bound with sulfides and organic matter, and the "residual" represented metals bound in the lattice structure of minerals. Nissenbaum (1972) used water, hydrogen peroxide, acetic acid, hydrochloric acid, and sodium carbonate fusion to sequentially release sediment metals that were considered to be water soluble, organic- and sulfide-bound, "exchangeable", carbonate- and hydrous oxide-bound, and silicate associated. Jenne et al. (1974) used sodium dithionite-citrate extraction to remove the Fe and Mn oxide fractions from sediments.

28. Engler et al. (1974) have incorporated a number of the above-mentioned extractants into a selective extraction scheme that provides an estimate of the metals bound within various sediment phases. Briefly, the method involved centrifugation and filtration to obtain interstitial water phase, ammonium acetate extraction for "exchangeable" phase, acidified hydroxylamine hydrochloride extraction for "easily reducible" phase, acidified 30% hydrogen peroxide digestion for "organic + sulfide" phase, sodium dithionite-citrate extraction for "moderate reducible" phase, and digestion with hydrofluoric, nitric, perchloric, and hydrochloric acids for the "residual" phase. The latter digestion step was later modified to use hydrofluoric, nitric, and fuming nitric acids (Brannon et al. 1976). Further modification of the overall method has been made by Chen et al. (1976).

29. Recently, Trefry (1977) used a sequential extraction scheme that employed squeezing of the sediments to remove interstitial water,

ammonium chloride extraction to remove "exchangeable" metal ions, sodium dithionite-citrate extraction for hydrous Fe and Mn oxides, sodium hypochlorite to oxidize organic matter followed by reduction of the resulting metal oxides with dithionite-citrate and, finally, hydrofluoric-perchloric acid digestion for the residual metals.

Generalizations Based Upon Literature

30. Based upon a review of the available literature, a number of generalizations can be made concerning the bioavailability of heavy metals to aquatic organisms. Among these are the following:

- (1) Heavy metals in solution vary over several orders of magnitude in their availability to benthic invertebrates. Some metals like Tl, Cs, and Ru are accumulated very slowly from solution while others like Zn, Cu, Cd, and Pb are accumulated rapidly and retained for a long time in the animal's tissues.
- (2) The accumulation potential of a metal, usually measured as the concentration factor (concentration in the tissues/concentration in the exposure water), may be affected by several physical and biological factors. Physical variables affecting the concentration factors of a metal include duration of exposure, the salinity or water hardness (for

fresh water), the exposure concentration, and the ambient temperature. Effects of these physical parameters vary from metal to metal.

- (3) Several biological factors are also important in heavy metals accumulation from solution. There are wide interspecies differences in concentration factors. Lamellibranch molluscs often have higher concentration factors for a given metal than do polychaete worms or crustaceans. Species differences are also seen within a phylum. Animal size and the stage in its life cycle also may affect heavy metals accumulation. Acclimation to environments high in heavy metals may increase or decrease the rates of uptake of different metals from solution.
- (4) The chemical form of a metal has an important effect on its bioavailability. For example, organic mercurials are generally accumulated more rapidly than inorganic mercury. A number of animals are able to transform a metal from one form to another thus changing its uptake/release kinetics.

- (5) Elevated concentrations of heavy metals in the tissues of benthic invertebrates are not always indicative of high levels of metals in the ambient medium or associated sediments. Use of these animals to monitor heavy metals pollution should be carried out with caution.
- (6) Heavy metals are often present at higher concentration in the tissues of animals from low-salinity environmental than in those from seawater. This relationship does not hold for all heavy metals and is probably related to differences in speciation and solubility characteristics of metals in fresh and saline waters.
- (7) The relationship between body weight and tissue heavy metal concentration varies from species to species and for different metals. In some cases, there are direct relationships between the two; in other cases, the relationship may be inverse or nonexistent.
- (8) Tissue heavy metals concentrations show seasonal variations in ambient heavy metals concentrations, ambient salinity and temperatures, or biological condition and physiological state of the animals.

- (9) Skeletal structures of benthic invertebrates may contain high concentrations of heavy metals. concentrations of metals in mollusc shells seem to be related to environmental factors (salinity and temperature) and to levels of the metals in the ambient medium. In crustaceans and squid, deposition of heavy metals in skeletal structures may be a means of sequestering and excreting potentially toxic metals.
- (10) Because several heavy metals are essential micronutrients to benthic invertebrates, they are actively accumulated from very dilute solution and their levels in the tissues are regulated in accordance with the needs of the animal. Since nutritional requirements for these metals vary, "normal" metals levels in tissues will vary from species to species.
- (11) For some heavy metals, there appears to be good correlation between metal concentration in the sediment and in the associated infaunal and epifaunal macrobiota. For other metals, no such correlation exists. These correlations often vary from one sediment to another. The

correlation, when it occurs, may be due to transfer of metals from sediment to biota or it may represent the presence of a common source of metals to both the sediment and biota.

- (12) Sediments naturally or artificially contaminated with radioisotopes of heavy metals have been used for studying metals uptake by benthic invertebrates. In some cases, uptake has been demonstrated; in others, it has not. The time required for equilibration of metals between sediments and the associated biota is long. Generally, accumulation of heavy metals from sediments, when it can be demonstrated, is several orders of magnitude less efficient than accumulation from aqueous solution.

PART III: METHODS AND MATERIALS

Collection of Sediment and Water Samples

31. Sediment samples were collected with an Ekman dredge, placed in precleaned plastic bags contained in 20-liter plastic containers, sealed, and stored in ice at 4°C for transport to the laboratory. Care was taken to minimize contact with air and to prevent possible contamination during collection and storage. Upon arrival at the laboratory, the samples were stored in refrigerators maintained at 2°C to 4°C until used. Bottom water samples for the elutriate test were also taken at the sample sites using a Kemmerer water sampler. These samples were placed in precleaned 3.8-liter plastic Cubitainers and returned to the laboratory for use.

32. During the initial phase of the study, samples were obtained from the Houston and Freeport, Texas, Ship Channels. Location of these sample sites as well as subsequent sampling sites along the Texas coast are shown in Figure 1. The Houston Ship Channel samples were collected 26 kilometers (km) above the point where the channel enters upper Galveston Bay and the Freeport samples were taken 8 km from the entrance of the Freeport Ship Channel to the Gulf of Mexico. All sediment and water sampling throughout this study was made at mid-channel locations. The Houston and Freeport samples were used for evaluation of the sediment extraction procedures used in subsequent tests. Some preliminary biological uptake studies were also made with these sediments but they were found to exhibit toxic properties to the organisms and their use was discontinued. Subsequently,

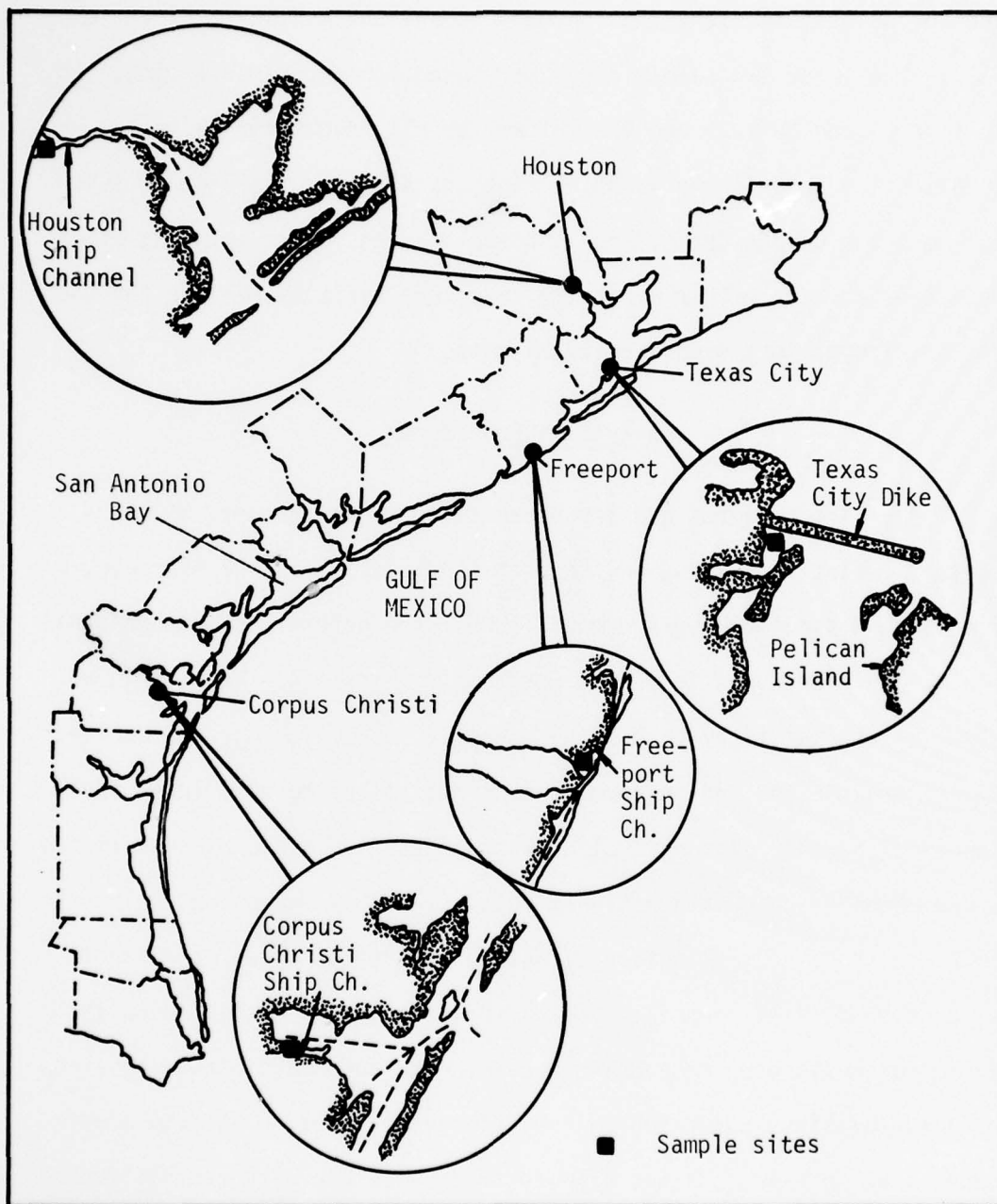


Figure 1. Sampling Locations along the Texas Coast

samples used in the biological tests were collected from the Texas City and Corpus Christi, Texas, Ship Channels and the Ashtabula River in Ohio. The first two sample areas were used for experiments conducted at 15‰ and 30‰ and the latter for all freshwater tests. Locations of these three sampling stations are shown in Figures 2-4. For both the Corpus Christi and Ashtabula areas, these sampling sites were used for the initial month-long exposure tests as well as for the second, longer term exposure experiments.

Analytical Procedures

33. The sediment quality parameters oil and grease, moisture content, volatile solids, pH, Eh, total sulfide, Kjeldahl nitrogen, and immediate dissolved oxygen demand (IDOD) were determined on each sediment using procedures in either Standard Methods, 14th Edition (APHA 1976) or the Chemistry Laboratory Manual - Bottom Sediments, compiled by the Great Lakes Region Committee on Analytical Methods (EPA 1969). The total organic carbon (TOC) content of the sediments was determined on an Oceanographic International Total Carbon System using their ampule method. Determination of sediment particle size according to percent sand, silt, and clay was by the sieve-pipet method (USGS 1973). Eh measurements were made using a Corning pH meter equipped with a combination platinum-saturated calomel electrode. Before Eh values were taken, the Eh electrode was allowed to equilibrate with the sediment for a period of 24 hours or until changes in measured Eh ceased.

34. Metals were determined using Perkin-Elmer Model 303 and Model 403 atomic absorption spectrophotometers equipped with D₂ arc

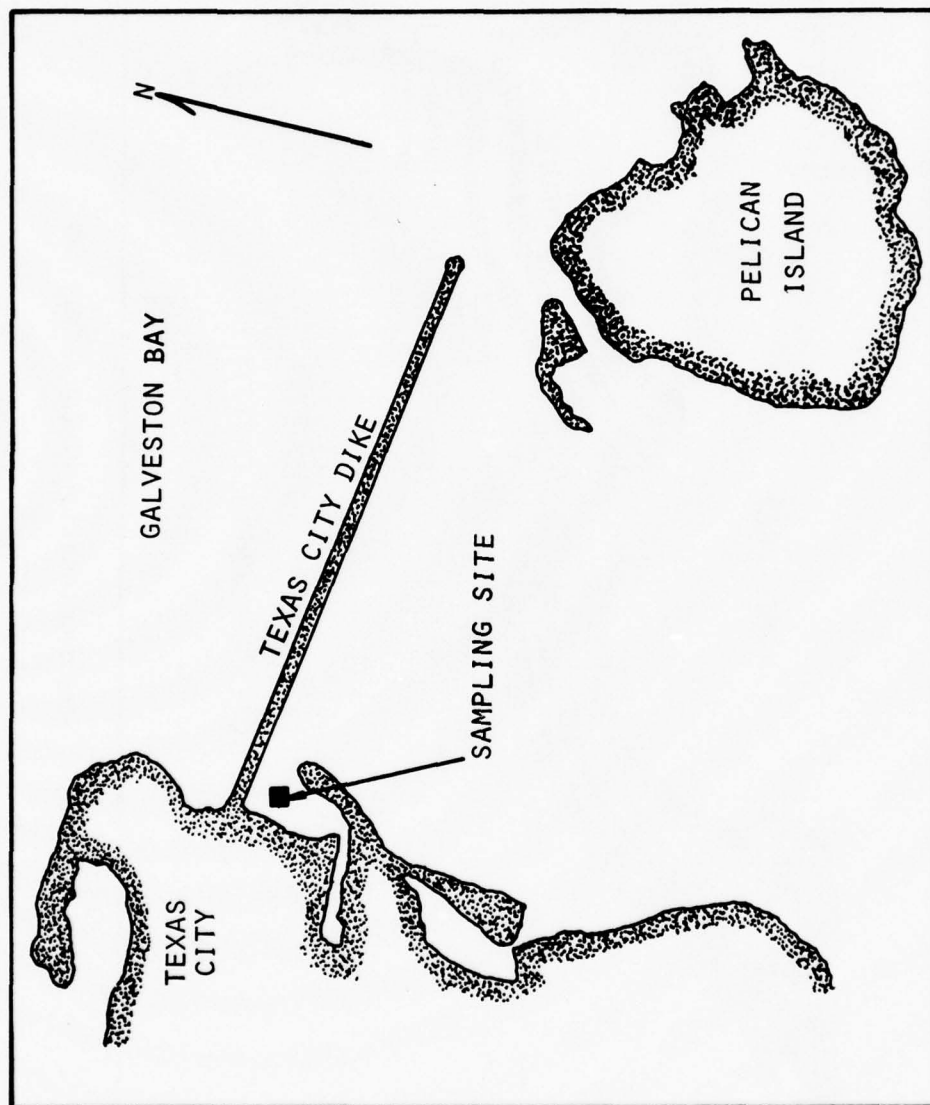


Figure 2. Sampling Location at Texas City

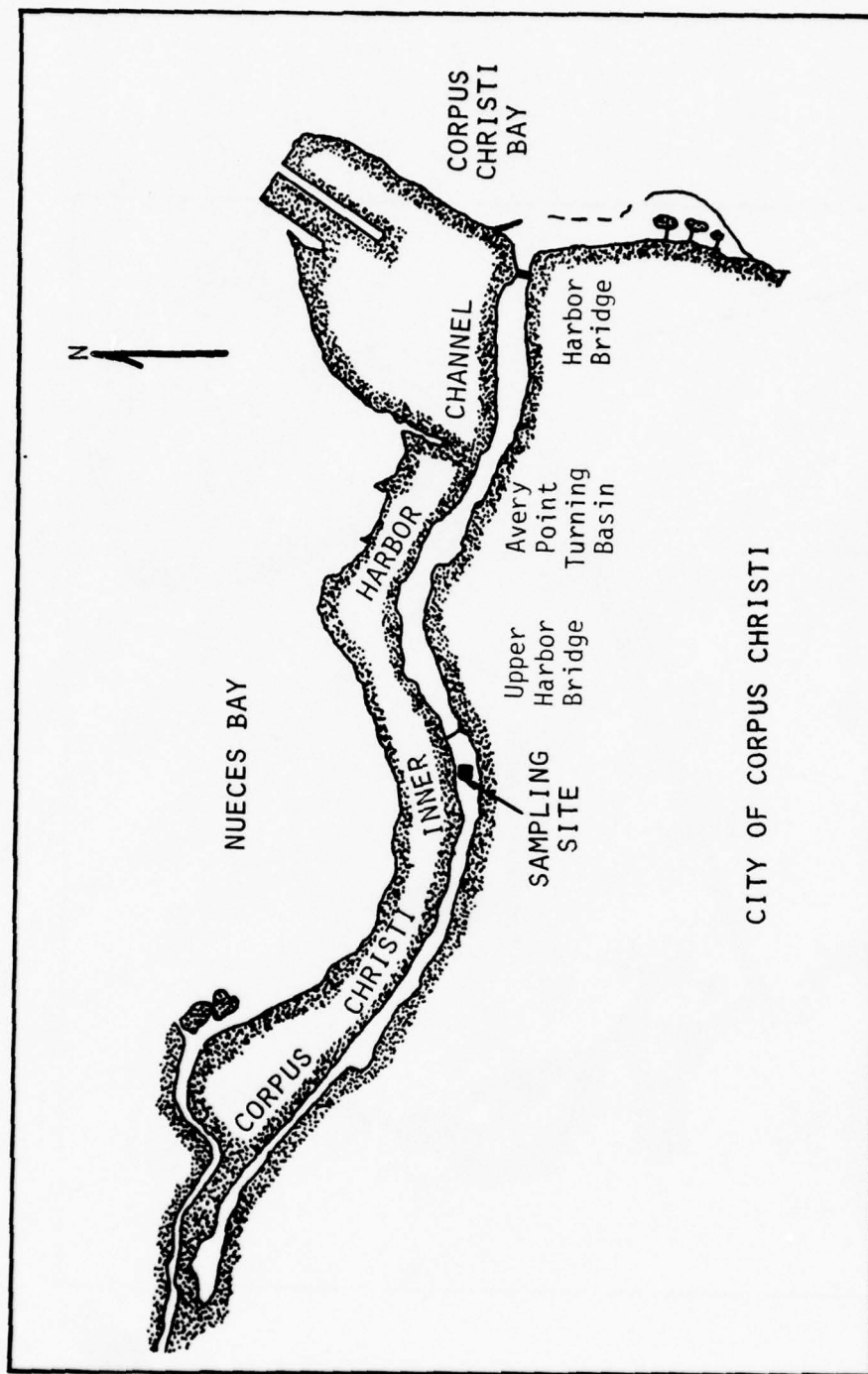


Figure 3. Sampling Location at Corpus Christi

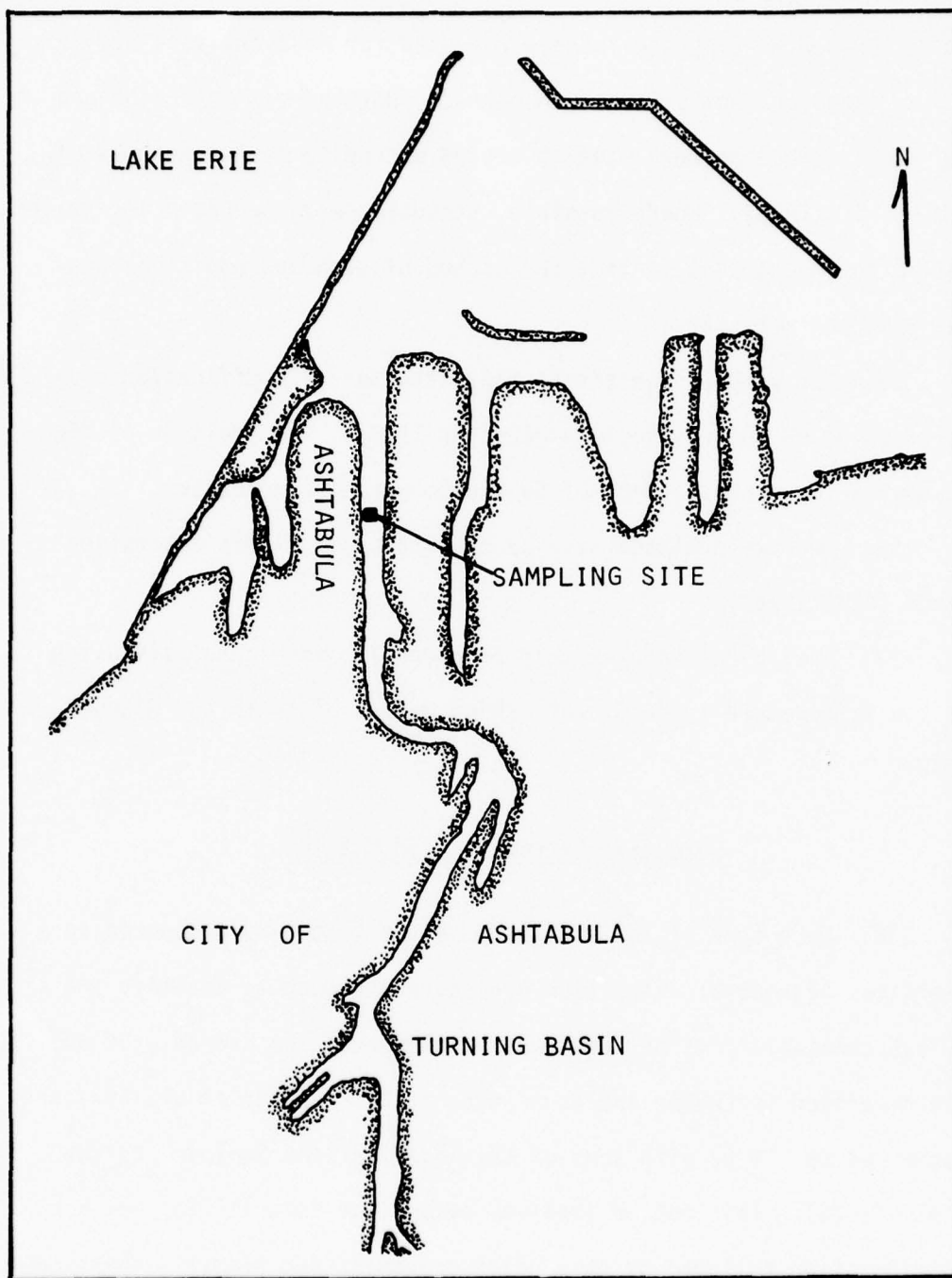


Figure 4. Sampling Location in Ashtabula River, Ohio

background corrector and Model HGA-2100 heated graphite atomizer. The Model 2100 heated-graphite furnace was used for most analyses due to the low metal concentrations encountered. Both direct injection and APDC-MIBK extraction were used as needed according to the methods of Chen et al. (1976). Where possible, standards were prepared in a matrix similar to the samples. Also, the method of standard additions was employed when necessary.

35. For samples containing NaCl, the matrix modification procedure using NH_3NO_3 was employed (Ediger 1975). The addition of NiNO_3 to samples for stabilization of Se and As was also necessary.

36. Mercury analyses were by the flameless atomic absorption method (APHA 1976).

37. Biological samples were prepared for metal analysis using the low temperature ($<300^\circ\text{C}$) wet ashing method of Smith and Windom (1972).

Selective Extraction for Metals

38. Each type of sediment used in the tests was subjected to a selective, sequential extraction procedure designed to identify the various chemical forms of heavy metals present. The method used was that developed by Engler and co-workers at WES (Engler et al. 1974 and Brannon et al. 1976) with some of the modifications employed by Chen et al. (1976). This method involved removal of interstitial water by centrifugation followed by sequential treatment and removal of various metal forms with the following chemical extractants: ammonium acetate,

hydroxylamine hydrochloride, acidic hydrogen peroxide, sodium dithionite, and a combination of hydrofluoric, nitric, and fuming nitric acids. A second set of extractions was also made using the same separations or extractants but in an individual, nonsequential manner. These were used to determine if a simple scheme involving individual extractants might be used to isolate or identify the form of heavy metals available to the benthic organisms. Initially, a total of 12 different extractants was evaluated using sediments obtained from the Houston and Freeport Ship Channels. Results of this study are discussed later. But briefly, they indicated that a number of these extractants gave approximately the same information on specificity and metal association with sediments and no additional information was obtained over that determined by the sequential extraction method reported by Engler and Brannon.

39. In addition to the above extraction procedures, each sediment used in these studies was subjected to the standard elutriate test prescribed by the EPA (1975).

Labware and Reagents

40. For the analysis of metals and their chemical forms in the test sediments, all containers used were made of Teflon, polypropylene, polyethylene, or tygon material. The labware, including sample storage containers, was precleaned by soaking with 1:1 nitric acid overnight and repeated rinsing with distilled-deionized water prior to use. All reagents were of the highest purity available. Baker "Ultrex" acids

were used and methyl isobutyl ketone (MIBK) was double-distilled grade. Ammonium pyrrolidine dicarbamate (APDC) was precleaned by solvent extraction before use.

41. Where exclusion of air or oxygen was desired, all manipulations involving the sediments and extractants were carried out inside polyethylene glove bags filled with commercially prepurified nitrogen further cleaned by passing through gas scrubbers filled with distilled-deionized water.

42. Metal standards used in these tests were prepared from Fisher Certified Atomic Absorption Standards and compared with EPA Trace Metal Reference Samples.

Biological Laboratory Tests

43. Laboratory uptake studies were conducted using sediments from the selected test sites. The availability of the metals in these sediments was investigated at 0, 15, and 30‰S.

44. Five species of benthic invertebrates were exposed to the various combinations of salinity and sediment. These included the estuarine clam *Rangia cuneata*, which was collected from San Antonio Bay, Texas, where the water is generally below 10‰S. The clams were acclimated to the desired salinity over a two to three week period prior to the start of an exposure. The clams were used at all three salinities and were exposed to all three sediments. The grass shrimp *Palaemonetes pugio* were exposed to Texas City and Corpus Christi sediments at both 15‰S and 30‰S. They were collected from Dickinson Bayou which empties into upper Galveston Bay, Texas. For the exposures

to Ashtabula sediment in fresh water, *Palaemonetes kadiakensis* was used. These small shrimp, very similar in appearance and size to *P. pugio*, were collected from Lake Somerville, Texas, and several feeder streams to the lake. This lake is located approximately 20 miles west of College Station, Texas. The polychaete *Neanthes arenaceodentata*, which is raised in the test laboratory from a culture originated by Dr. Donald Reish, California State University, Long Beach, was exposed to the Texas City and Corpus Christi sediments at 30‰S. The oligochaete *Tubifex* sp., purchased from C & C Fisheries, Portland, Oregon, was exposed to Ashtabula sediment in fresh water.

45. There were two experimental designs employed during the course of the study. For the short-term exposures, 5.6-liter polyethylene buckets were used for both experimental and control chambers. Prior to introducing the sediment into the experimental containers, it was mixed under nitrogen at 5°C to insure homogeneity. Approximately 2.5 liters of sediment and 2.5 liters of the desired salinity water were transferred to the experimental chambers. The sediment was allowed to equilibrate for 24-48 hours prior to the introduction of the organisms. Gentle aeration was supplied to the water in each container with air that was first bubbled through a 50% NaOH solution and then distilled water. The control chambers contained the same salinity water as the experimental ones but did not contain any sediment.

46. With a few exceptions, sampling for the short-term tests was conducted on days 2, 4, 8, 16, and 32 of exposure. Three replicate chambers of both experimental and control animals were set up for each

sampling date. For tests involving either *Tubifex* or *Neanthes* sp., 20-cm finger bowls were used as exposure chambers. The control chambers contained a clean sand substrate. In the first tests with the Texas City sediment, all chambers were monitored daily for Eh, pH, and O₂ concentrations. Very little change was noted, so in subsequent tests this monitoring was discontinued. All experiments were conducted under controlled light (8 hours dark, 16 hours light) and temperature (20°C ± 2°C) conditions.

47. Five *Rangia* and approximately 20-25 *Palaemonetes* were held in each experimental and control chamber. The shrimp were fed chopped shrimp which had been maintained under control conditions, but the clams were not provided with an additional food supply. Approximately 25 *Neanthes* were placed in each 20-cm finger bowl. The *Tubifex* were not counted but a sufficient number was used to insure an adequate quantity for analysis. Day 0 animals were taken for analysis before every test. At the specified sampling time, water samples were taken and the animals were removed from each of the replicate chambers for that date. All animals were rinsed in distilled water to remove sediment residues and in the case of clams shucked. They were then sealed in plastic bags and frozen at -60°C until the tissue was analyzed for metals. Both species of worms were placed in clean water for 24 hours after removal from the sediment so that their guts would be purged of sediment prior to analysis. After the 24-hour purge time, the worms were rinsed and frozen.

48. The second experimental design, used during the last 9 months

of the investigation, employed 208-liter rectangular fiberglass tanks for the experimental and control chambers. A substrate of clean sediment was used for both the experimental and control tanks. For freshwater tests, sediment collected from Lake Somerville was used as the substrate. For tests involving 15‰ and 30‰ water, the substrate was sediment from San Antonio Bay. The volume of substrate used was 3-5% of the volume of the tank. After the substrate had been added, the tanks were filled with the desired salinity water and aerated. The chambers were allowed to equilibrate for 24 hours prior to introducing the animals. Between 70-75 clams and 300-400 shrimp were placed in each control and experimental tank. Prior to the introduction of the test sediment, it was mixed to insure homogeneity. A slurry was made using one part sediment to four parts water and this mixture was introduced into the water column over a 15-minute period. The amount of sediment used to make the slurry was approximately 3% of the volume of the tank. As in the previous tests, shrimp were fed shrimp, but it was also noticed that the shrimp fed on dead clams.

49. The sampling times were every week for 4 weeks and then every 2 weeks for the remainder of the exposure period. Water samples were taken at every sampling interval and animals were frozen for analysis as described earlier. Tests using *Neanthes* and *Tubifex* utilized the same experimental design as in previous tests except that a substrate of relatively metal-free sediments was used and the test sediment was layered over this.

50. Depuration tests were performed on all organisms exposed to

Corpus Christi sediment, as well as some of those exposed to Texas City and Ashtabula sediments. These tests involved removal of a number of organisms from the test sediments after 8 days exposure and transfer to containers containing clean water of the same salinity. After 2 and 8 days of depuration in sediment-free water, the animals were sacrificed and analyzed for heavy metals as described above.

51. An analysis of variance (ANOVA) was performed on the heavy metal uptake data using the General Linear Models (GLM) procedure of Statistical Analysis Services, Inc. (Barr et al. 1976). Statistical analyses were performed with the Amdahl 470-6 computer at Texas A&M University. The GLM procedure allows ANOVA of data sets containing different numbers of data points. The probability level used to determine significance was 0.05.

52. A 2-way ANOVA was performed on the data for *Neanthes arenaeodentata* exposed to Texas City and Corpus Christi sediments, in short-term exposures, for all animals exposed to Ashtabula sediment, and for all the longer term exposures. In these cases, the animals were exposed to the sediment at only one salinity, yielding 2 variables for ANOVA, exposure and duration of exposure. The significance of the main effects and, where justified, their interaction on metals uptake was assessed. The short-term experiments, *Rangia cuneata* and *Palaemonetes pugio* were exposed to Texas City and Corpus Christi sediments at 2 salinities, yielding a 3-factor design. A 3-way ANOVA was performed on these data. The significance of the main factors, exposure, time, and salinity as well as the 3 first-order interactions

were assessed. Because of the nature of the data, an analysis of second-order interactions did not seem justified. Where 2 or 3 of the 2-way interactions are not significant, it is extremely unlikely that the 3-way interaction will be significant (Steel and Torrie 1960). In the majority of investigations in which the effects of 3 independent variables on a biological process are investigated, a model which excludes the 3-way interactions adequately describes the data (Alderdice, 1963; 1972; Alderdice and Forrester, 1971). In the 3 instances in which 2 or 3 of the 2-factor interactions were statistically significant, the R^2 statistic was 0.853, 0.993, and 0.998, indicating that the main factors and their 2-way interactions adequately described the variation in the data.

PART IV. RESULTS

Evaluation of Sediment Extractants

53. The early stages of this study were devoted to selection of a number of extractants that could be used to identify the chemical and physical forms or phases in which metals are located within sediments. This was accomplished by subjecting test sediments from the Houston and Freeport Ship Channels to a series of physical separations or chemical extractions that might reasonably be expected to indicate the forms of metals present. Among these were the following:

- (1) Centrifugation to remove interstitial water - provide an idea of the amount of water soluble metals in the sediment.
- (2) Distilled deionized water extract - same as (1) except no salts existing in solution and therefore minimal "salt effect" on solubility.
- (3) 15‰ and 30‰ sodium chloride extract - indication of metals soluble in marine waters.
- (4) Neutral 1N ammonium acetate extract - an indication of "ion exchangeable" metals.
- (5) Calcium chloride (0.1M) extract - same as (3).
- (6) Acidic hydrogen peroxide (30%) extract - removes organic bound metals, also sulfide bound.
- (7) Hydroxylamine hydrochloride (0.1M) extract - frees metals occluded or sorbed on hydrous oxides that are easily reduced.

- (8) Sodium dithionite-citrate extract - same as (6) except from more moderately reduced oxides.
- (9) Diethylenetriamine pentaacetic acid extract - used to estimate "available" metals in soil.
- (10) Acetic acid (1M) extract - removes carbonate sorbed metals, also some oxide occluded.
- (11) Nitric, hydrofluoric, and fuming nitric acid digestion - estimate of total metals present.

A brief description of each method is presented in Appendix B.

54. The physical and chemical characteristics of the test sediments are given in Table 1 and the test results presented in Tables 2 and 3 as percent of the total metal extracted. Also included for comparison are the results obtained using the sequential extraction procedure of Engler et al. (1974). The metal phases isolated by the latter were interstitial water (IW), exchangeable phase (EP), easily reducible phase (ERP), organic plus sulfide phase (OSP), moderately reducible phase (MRP), and residual phase (RP). During this phase of the study, difficulty was encountered in obtaining dithionite of sufficient purity (even after further purification in the laboratory) to determine the MRP or carry out the dithionite extraction individually. As a result, this step was omitted and the results in Tables 2 and 3 give the MRP combined with the RP.

55. As expected, a number of the extractants provided essentially the same information as to metal form or phase and the number of extractants used in subsequent tests was reduced to include only interstitial water, ammonium acetate, acetic acid, hydroxylamine hydrochloride, acidic

Table 1
Physical and Chemical Quality
Houston and Freeport Sediments

<u>Sediment Characteristic</u>	<u>Houston Ship Channel</u>	<u>Freeport Ship Channel</u>
Eh (mv)	-230	-208
pH	6.7	7.1
Moisture Content (%)	64	50
Volatile Solids (%)	7.3	5.7
Particle Size		
% Sand	0	2
% Silt	48	39
% Clay	52	59
IDOD (mg/kg)	1,190	445
Oil & Grease (mg/kg)	1,033	1,365
TOC (%)	1.8	1.4
Cu (mg/kg)	73	87
Cr (mg/kg)	137	44
Cd (mg/kg)	6.1	2.1
Fe (mg/kg)	33,500	15,900
Ni (mg/kg)	51	44
Mn (mg/kg)	582	477
Pb (mg/kg)	207	46
Zn (mg/kg)	555	201

Table 2
Extraction Efficiency Houston Ship Channel Sediments
 (Percent of Total Metal)

Extractant or Phase	Cu	Zn	Pb	Cd	Ni	Mn	Fe	Cr
H ₂ O	0.12	0.16	0.04	0.26	0.02	0.16	0.13	0.06
15°/∞NaCl	0.06	0.16	0.01	0.12	0.01	0.28	0.04	0.23
30°/∞NaCl	<0.02	0.18	<0.01	0.23	<0.01	0.60	0.02	0.12
CaCl ₂	0.08	0.29	0.02	<0.02	<0.01	3.3	0.07	<0.01
NH ₄ Ac	0.03	0.31	0.03	0.23	0.33	7.0	0.78	0.02
DTPA	0.03	1.17	0.41	4.1	1.6	15.3	0.92	0.07
HAc	<0.02	12.4	0.77	0.88	8.0	30.9	32.0	12.4
NH ₂ OH	<0.02	38.7	21.3	15.2	11.8	29.2	27.4	21.2
HCl	0.18	37.3	1.2	2.3	11.2	32.3	38.0	16.0
H ₂ O ₂	82.2	57.1	99.0	72.1	31.4	35.9	14.4	51.8
IW	<0.02	0.03	<0.01	0.02	<0.01	0.18	<0.01	<0.01
EP	0.01	0.06	0.03	0.03	0.20	4.5	0.45	0.01
ERP	0.26	30.3	5.3	3.1	6.9	19.2	20.7	13.8
OSP	52.9	35.6	80.0	58.5	17.6	11.9	6.8	32.8
MRP+RP	33.1	14.4	5.0	10.3	28.4	11.2	51.2	51.1

Table 3
Extraction Efficiency Freeport Ship Channel Sediments
(Percent of Total Metal)

Extractant or Phase	Cu	Zn	Pb	Cd	Ni	Mn	Fe	Cr
H ₂ O	0.05	0.28	0.02	0.19	0.01	0.09	0.01	0.11
15°/°NaCl	0.03	0.28	0.09	<0.05	0.01	0.05	0.01	0.04
30°/°NaCl	0.08	0.28	<0.04	0.24	0.01	0.17	<0.01	0.11
CaCl ₂	0.02	0.33	0.09	<0.05	<0.01	0.65	<0.01	<0.02
NH ₄ Ac	<0.02	0.38	0.33	1.7	0.34	3.6	0.03	0.02
DTPA	0.08	0.28	1.3	24.8	0.52	5.7	0.24	0.14
HAc	<0.02	11.9	1.4	10.0	9.8	33.3	32.2	4.3
NH ₂ OH	<0.02	46.8	11.7	6.2	10.2	31.7	26.9	3.9
HCl	0.13	3.6	0.67	6.7	7.5	36.0	34.9	34.1
H ₂ O ₂	64.4	79.1	82.6	34.3	31.8	53.0	24.0	19.5
IW	<0.02	0.04	0.04	0.29	<0.01	0.17	0.01	0.02
EP	0.03	0.13	0.13	0.33	0.25	3.6	0.13	0.05
ERP	0.09	42.0	2.9	0.81	9.0	27.8	17.4	2.7
OSP	78.9	67.5	88.4	43.6	27.9	24.2	30.4	19.2
MRP+RP	30.6	39.7	14.0	11.0	30.3	21.5	80.7	99.9

hydrogen peroxide, and nitric-hydrofluoric-fuming nitric acids. In addition, the sequential extraction procedure and the standard elutriate test was made on each sediment used in the biological tests.

Characterization of Test Sediments

56. Sediment quality characteristics of the three test sediments used in the main biological uptake studies are given in Table 4. These *sediments were predominantly fine grained silty clays existing in reducing environments ($E_h < -100$ mv) and near neutral pH. They contained from 1 to 2% organic carbon with the Texas City sediment having the highest TOC. This was also reflected in the oil and grease content (0.5%) of this sediment. The Corpus Christi sediment was lowest in organics and highest in sulfide. The quality parameters suggest that the two marine sediments were sufficiently different so as to have provided different matrices and thereby different available forms of metals for the uptake studies.*

57. Total concentration levels of heavy metals in all three sediments are shown in Table 5. For most metals the levels are considerably higher than those of natural background sediments found along the Texas Coast (Slowey et al. 1973).

58. Results of the standard elutriate test for 9 of the metals are given in Table 6. These indicate that manganese, mercury, and iron were the only significant releases to the water during the tests for Texas City and Ashtabula sediments. For sediments from Corpus Christi, zinc and lead were released in addition to manganese, mercury, and iron.

Table 4
Sediment Quality Parameters

<u>Parameter</u>	<u>Texas City Channel</u>	<u>Corpus Christi Channel</u>	<u>Ashtabula River</u>
Eh	-220.0	-148	-118
pH	7.8	7.2	7.0
Moisture Content (%)	67	50	38
Volatile Solids (%)	7.1	6.2	6.9
Particle Size			
% Sand	0	6	<1
% Silt	22	32	18
% Clay	78	62	81
IDOD (mg/kg) (15 min.)	2,526	850	1,184
Oil & Grease (mg/kg)	4,890	655	772
TOC (%)	1.8	1.0	1.1
Kjeldahl N (mg/kg)	1,512	970	1,456
$\Sigma S^{=}$ (mg/kg)	980	1,528	250

Table 5
Total Concentration of Metals in Sediments

Total Concentration, mg/kg of Dry Weight			
Element	Texas City Channel	Corpus Christi Channel	Ashtabula River
Cu	48	120	37
Cr	188	82	175
Cd	2.4	21	4.8
Fe	14,500	12,300	27,300
Ni	48	17	52
Mn	570	257	356
Pb	41	316	42
Zn	161	4055	315
Hg	0.6	18	1.1
V	136	-	222

Table 6
Elutriate Test Results

METAL	TEXAS CITY		ASHTABULA		CORPUS CHRISTI	
	Site water ($\mu\text{g}/\ell$)	Elutriate ($\mu\text{g}/\ell$)	Site water ($\mu\text{g}/\ell$)	Elutriate ($\mu\text{g}/\ell$)	Site water ($\mu\text{g}/\ell$)	Elutriate ($\mu\text{g}/\ell$)
Cu	20	9	8	6	9	3
Zn	44	28	85	50	325	1700
Mn	32	5800	3	550	22	890
Fe	44	52	15	650	10	20
Pb	1	1	1	1.5	2	6
Cr	7	6	<5	<5	<5	<5
Cd	<1	<1	<1	<1	<1	<1
Ni	85	75	21	20	11	9
Hg	0.05	0.10	0.11	2.86	<0.05	0.55

59. Results of the sequential and nonsequential extractions are given in Tables 7 through 12. As indicated in Table 7, highest metals found in the Texas City interstitial water were manganese and iron with a trace of zinc. These metals also dominated the EP although the amount present was only a small fraction ($<0.5\%$) of the total metals present with the exception of Mn, which had about one-third of its total present in the EP. More than one-half of the Mn was associated with the easily reducible phase with the remainder distributed between the OSP and RP. About 18% of the Fe was also associated with ERP with the remaining Fe being distributed equally between the OSP, MRP, and RP. With the exception of Ni and Cd, the remaining metals were associated to a large extent with the OSP. The Ni and Cd were primarily contained in the RP. Results of the non-sequential extractions are given in Table 8.

60. Results for the Ashtabula sediments (Tables 9 and 10) were similar to those obtained for Texas City in that Mn and Fe constituted the more abundant metals in the IW with traces of the other metals. Again, the predominant Mn association was with the ERP with a lesser but substantial amount present in the OSP. Contrary to the Texas City sediment, the bulk of the Fe in Ashtabula sediment was associated with the OSP. Similarly, the remaining metals were largely contained in the OSP.

61. The second estuarine or marine sediment used (Corpus Christi) differed from the Texas City sediment in that there appeared to be less readily available metals present as indicated by the very low metal levels in the IW and EP (Tables 11 and 12). It should, however, be remembered that the elutriate test suggests that with mixing at least

Table 7
Sequential Extracts of Texas City Channel Sediments

Phase	Heavy Metals, mg/kg							
	Cu	Zn	Pb	Cr	Fe	Mn	Ni	Cd
IW	0.02	0.12	<0.01	0.01	0.2	12.	0.001	0.002
EP	0.02	0.26	<0.01	0.05	69.	182.	0.011	0.001
ERP	0.10	10.0	<0.1	4.3	2,550.	389.	1.25	0.009
OSP	31.0	77.0	29.0	97.0	5,056.	135.	9.9	0.81
MRP	0.10	-*	-	<5	4,250.	10.	3.0	-
RP	13.0	109.0	7.9	69.0	5,075.	82.	28.0	1.5
Sum of Above	44	196	37	170	17,000	810	42	2.3

*Indicates data not valid due to high reagent blank

Table 8
Non-sequential Extracts of Texas City Channel Sediments

Extractant	Heavy Metals, mg/kg							
	Cu	Zn	Pb	Cr	Fe	Mn	Ni	Cd
Interstitial Water*	0.02 0.02	0.12 0.13	<0.01 <0.01	0.01 0.01	0.2 0.2	12. 12.	0.001 0.001	0.002 0.002
NH ₄ Ac	0.01	0.32	0.02	0.07	85.	194.	0.015	0.020
HAc	0.10	24.	1.8	16.9	4,520.	536.	2.1	0.014
NH ₂ OH	0.14	25.	1.3	13.9	4,480.	550.	1.8	0.028
H ₂ O ₂	20.	48.	11.3	58.	9,040.	360.	5.9	0.37
Total (HNO ₃ -HF)	48.	161.	41.	188	14,500	570	48.	2.4

*Second Interstitial Water Values in µg/ml

Table 9
Sequential Extracts of Ashtabula River Sediments

Phase	Heavy Metals, mg/kg							
	Cu	Zn	Pb	Cr	Fe	Mn	Ni	Cd
IW	0.006	0.04	0.001	0.007	8.	1.	0.001	0.001
EP	0.01	0.2	0.007	0.04	397.	30.	0.043	0.006
ERP	0.08	60.	1.8	21.	5,123.	335.	6.2	0.16
OSP	33.	190.	37.	114.	19,410.	218.	28.	5.7
MRP	1.2	-*	-	-	2,540.	8.	1.1	-
RP	5.9	46.	8.5	64.	9,410.	39.	19.	<0.1
Sum of Above	40	296.	47.	199.	36,888.	631.	54.	5.9

*Indicates data not valid due to high reagent blank

Table 10
Non-sequential Extracts of Ashtabula River Sediments

Extractant	Heavy ($\mu\text{g/gm}$) Metals, mg/kg							
	Cu	Zn	Pb	Cr	Fe	Mn	Ni	Cd
Interstitial Water*	0.006	0.04	<0.01	0.007	8.	1.	0.001	0.001
	0.020	0.14	<0.01	0.023	27.	3.	0.003	0.003
NH ₄ Ac	0.01	0.22	0.008	0.04	423.	35.	0.008	0.050
HAc	0.10	68.	2.6	28.	6,970.	330.	7.6	0.062
NH ₂ OH	0.08	79.	3.1	25.	6,080.	300.	7.8	0.30
H ₂ O ₂	33.	213.	37.	105.	19,410.	356.	46.	4.6
Total (HNO ₃ -HF)	37.	315.	42.	175.	27,350	450.	52.	4.8

*Second Interstitial Water Values in $\mu\text{g/ml}$

Table 11
Sequential Extracts of Corpus Christi Sediments

Phase	Heavy Metals, mg/kg							
	Cu	Zn	Pb	Cr	Fe	Mn	Ni	Cd
IW	0.01	0.10	0.15	0.01	0.04	0.4	0.006	0.004
EP	<0.01	0.08	0.05	0.04	0.5	9.6	<0.02	<0.001
ERP	<0.1	117.	0.6	0.14	235.	108.	0.22	0.02
OSP	88.	410.	286.	58.	3,115.	146.	5.1	21.
MRP	29.	185.	6.	9.	1,685.	15.	1.2	<0.1
RP	10.	145.	18.	21.	7,495.	15.	7.1	3.0
Sum of Above	127.	4547.	311.	88.	12,350.	294.	14.	24.

Table 12
Non-sequential Extracts of Corpus Christi Sediments

Extractant	Heavy Metals, mg/kg							
	Cu	Zn	Pb	Cr	Fe	Mn	Ni	Cd
Interstitial Water*	0.008	0.10	0.14	0.009	0.035	0.4	0.006	0.004
	0.010	0.12	0.18	0.011	0.045	0.5	0.008	0.005
NH ₄ Ac	<0.01	<0.05	0.18	0.055	1.16	11.8	<0.02	<0.001
HAc	<0.1	715.	2.3	5.5	1,030.	200.	0.70	<0.01
NH ₂ OH	<0.1	88.	0.61	0.9	330.	142.	0.47	0.01
H ₂ O ₂	189.	4,410.	352.	70.	2,200.	315.	4.2	20.
Total (HNO ₃ -HF)	120.	5,041.	316.	82.	11,290.	257.	14.	21.

*Second Interstitial Water Values in µg/ml

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TEXAS A AND M RESEARCH FOUNDATION COLLEGE STATION

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AVAILABILITY OF SEDIMENT-ADSORBED HEAVY METALS TO BENTHOS WITH --ETC(U)

AUG 78 J W NEFF, R S FOSTER, J F SLOWEY

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four of the metals in the Corpus Christi sediment were readily released to the water. Due to the high sulfide level and low Eh of this sediment, it appears reasonable to assume that the zinc and lead are not released until some oxygenation, as in the elutriate test, occurs. However, it was expected that iron and manganese would be somewhat soluble in the interstitial waters of such sediments but this was not found. A substantial portion of all metals were contained in the OSP except Fe and Ni which were mostly in the RP.

62. One of the major problems with use of acidic hydrogen peroxide as an extractant is that we cannot differentiate between organic bound metals and metal sulfides. Quality of Texas City sediments suggests that the OSP might be organic although some sulfide association cannot be ruled out. The same may be said for Ashtabula sediments. However, in those from Corpus Christi, the OSP most probably represents metal sulfides. A similar interpretation for metal distribution in the Corpus Christi area was made by Holmes et al. (1974).

63. It is difficult to provide specific detection limits for metals within the various fractions determined since the amount of material varied from test to test. However, general detection limits were: Cd, 1 $\mu\text{g/l}$; Cr, 5 $\mu\text{g/l}$; Cu, 1 $\mu\text{g/l}$; Fe, 5 $\mu\text{g/l}$; Hg, 0.05 $\mu\text{g/l}$; Mn, 3 $\mu\text{g/l}$; Ni, 5 $\mu\text{g/l}$; Pb, 1 $\mu\text{g/l}$; and Zn, 1 $\mu\text{g/l}$.

64. Precision of the metal analyses in this study were within the following ranges: <5% (Cu, Mn, Zn), 5-10% (Pb, Hg, Fe), and 10-15% (Ni, Cr, Cd).

Bioaccumulation Studies

65. Results for uptake of 10 metals by individual organisms exposed to test sediments are presented below. Statistical analysis of this data is given in Appendix Tables A1 through A19.

Iron (Fe)

66. Statistical analyses of Fe accumulation by all species are summarized in Table A1.

67. *Rangia cuneata*. The main effects of salinity and time, but not of exposure to sediment or of any of the two-way interactions, had a significant effect on the concentration of Fe in the tissues of clams *Rangia cuneata* exposed to Texas City sediment at 15‰ and 30‰. This indicates that the temporal pattern of tissue Fe concentrations were different at the two salinities. The lack of significance for the main effect of exposure was due to the large variability in Fe levels in clams at different times, particularly at 15‰. At 15‰, mean Fe concentrations in control clams varied between 159 mg/kg and 194 mg/kg (dry weight) during the time course of the experiment, while mean Fe concentrations in sediment-exposed clams rose to 356 mg/kg on day 4 and then declined steadily thereafter to a mean of 182 mg/kg at the end of the exposure period (Figure 5)*. At 30 ‰, mean tissue Fe concentrations in control clams were lower and less variable (128 mg/kg to 164 mg/kg) (Figure 6). In the sediment-exposed group,

* In all figures, vertical bars represent 1 standard deviation. Where bars are missing, the standard deviation is smaller than the size of the symbol.

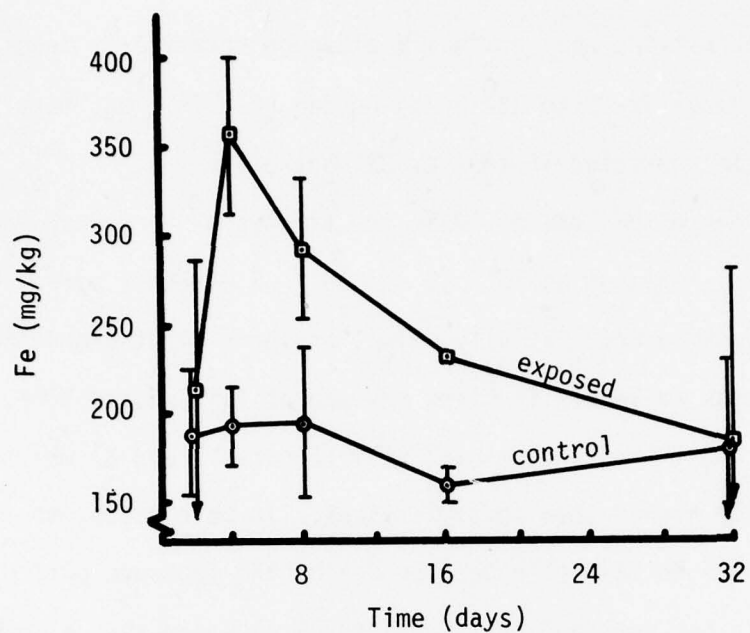


Figure 5. Mean Fe Uptake by *Rangia cuneata* Exposed to Texas City Sediment at 15‰ S

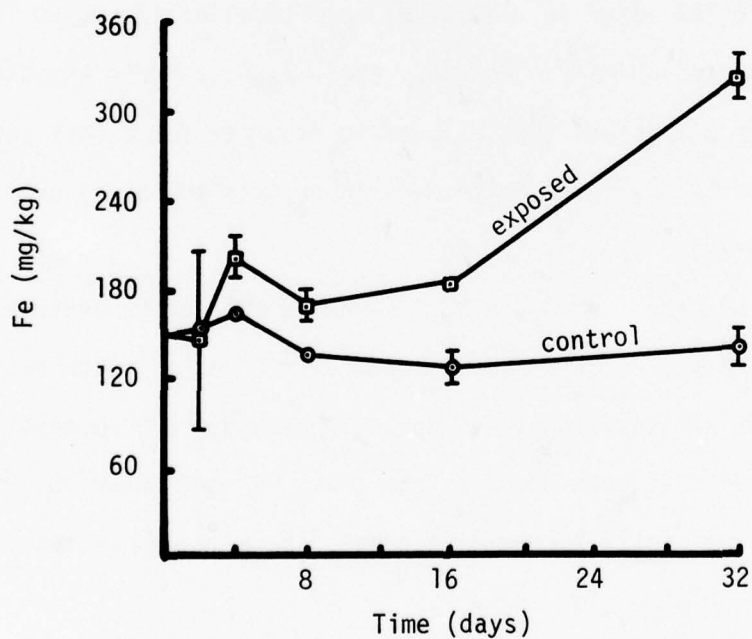


Figure 6. Mean Fe Uptake by *Rangia cuneata* Exposed to Texas City Sediment at 30‰ S

tissue Fe concentrations rose gradually although erratically from a mean of 148 mg/kg on day 0 to 332 mg/kg on day 32. This was more than double the Fe concentration in the day 32 controls.

68. The concentrations of Fe in the tissues of *R. cuneata* exposed to Corpus Christi sediment at 15‰ and 30‰ were not affected significantly by exposure, salinity, time, or their first-order interactions. Final mean Fe levels in clams exposed at 15‰ and 30‰ were 151 mg/kg and 137 mg/kg, respectively (Figures 7 and 8) which was not significantly higher than control values. In both cases, there was a trend for tissue Fe levels to decline during the exposure period. Clams exposed to the sediment at 15‰ for 8 days and then allowed to depurate in sediment-free seawater for the same length of time contained a mean of 144 mg/kg Fe, below the mean level of 178 mg/kg found in the 8-day exposed animals. However, at 30‰, animals exposed to the sediment for 8 days and then allowed to depurate for 8 days contained a mean of 146 mg/kg Fe which was higher than the 8-day exposed level of 137 mg/kg.

69. As indicated in Figure 9, *R. cuneata* exposed to Ashtabula sediment in fresh water contained higher mean tissue Fe concentrations than controls at all sampling times during the exposure. Regression analysis revealed that both exposure and time, but not their interaction, contributed significantly to the differences in Fe levels between control and exposed clams.

70. Tissue Fe concentrations in control clams remained relatively constant and below 400 mg/kg at all sampling times (Figure 9). In the

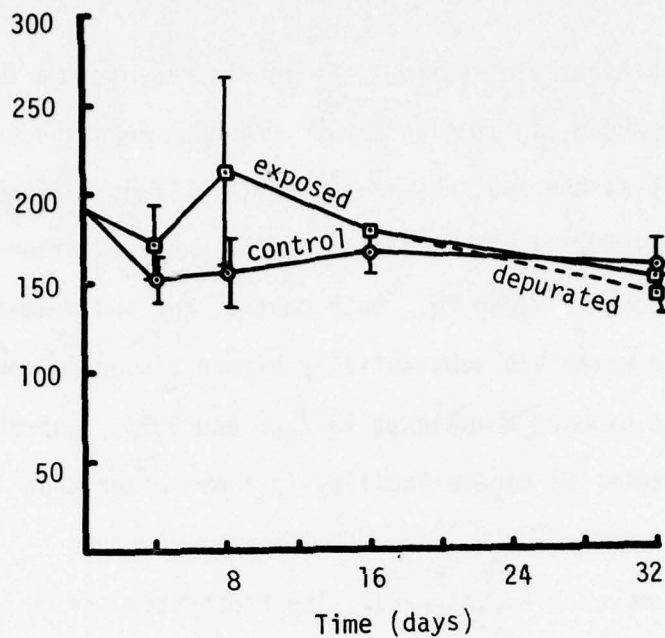


Figure 7. Mean Fe Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 15‰S

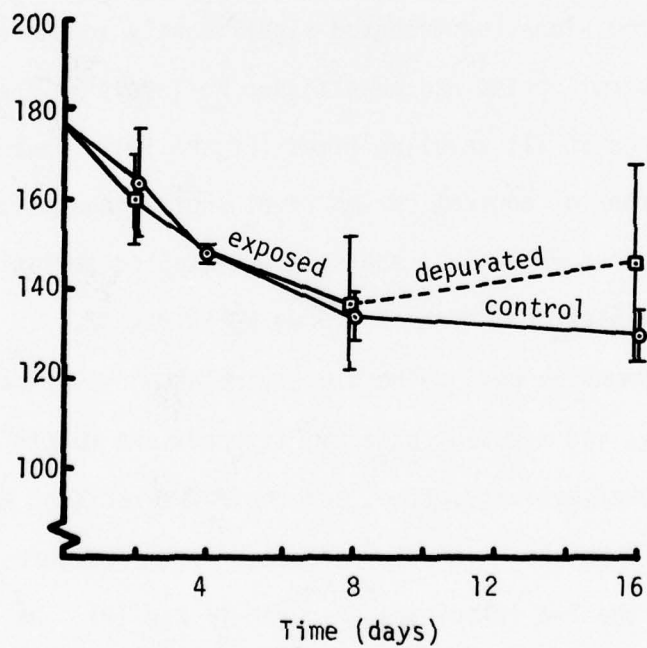


Figure 8. Mean Fe Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 30‰S

clams exposed to Ashtabula sediment, Fe levels rose from a day 0 value of 220 mg/kg to 780 mg/kg at five days. The mean Fe concentration then dropped slightly at the two subsequent sampling times and then rose to 2110 mg/kg at day 20. A single tissue sample analyzed after 32 days exposure contained 710 mg/kg Fe. Both control and sediment-exposed animals in fresh water had substantially higher tissue Fe concentrations than control and exposed animals at 15‰ and 30‰, probably reflecting a greater Fe bioavailability in fresh water than in seawater.

71. *Palaemonetes kadiakensis*. The freshwater shrimp *P. kadiakensis* also showed a significant accumulation of Fe from Ashtabula sediment in fresh water. Exposure and the interaction of exposure and time, but not time alone, contributed significantly to the observed uptake. The control shrimp had mean tissue Fe levels in the 40 mg/kg to 100 mg/kg range at all sampling times (Figure 10). There was an insufficient number of control shrimp remaining for analysis at 32 days. The Fe concentrations in the sediment-exposed shrimp rose in a nearly steady fashion to a high of 610 mg/kg at day 32.

72. *Palaemonetes pugio*. The closely related estuarine grass shrimp, *P. pugio*, was exposed to Texas City sediment at both 15‰ and 30‰. Exposure, salinity, time, and their interactions had a significant effect on Fe uptake. This is reflected in the patterns of Fe accumulation at the two salinities (Figures 11 and 12). At both 15‰ and 30‰, the highest level of tissue Fe was reached in sediment-exposed animals at the day 2 sampling time (235 mg/kg and 106 mg/kg,

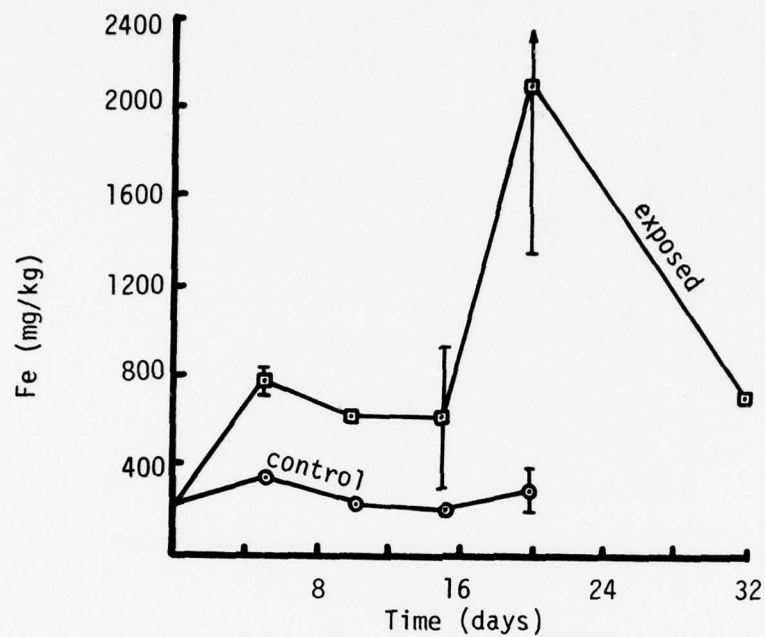


Figure 9. Mean Fe Uptake by *Rangia cuneata* Exposed to Ashtabula Sediment in fresh water

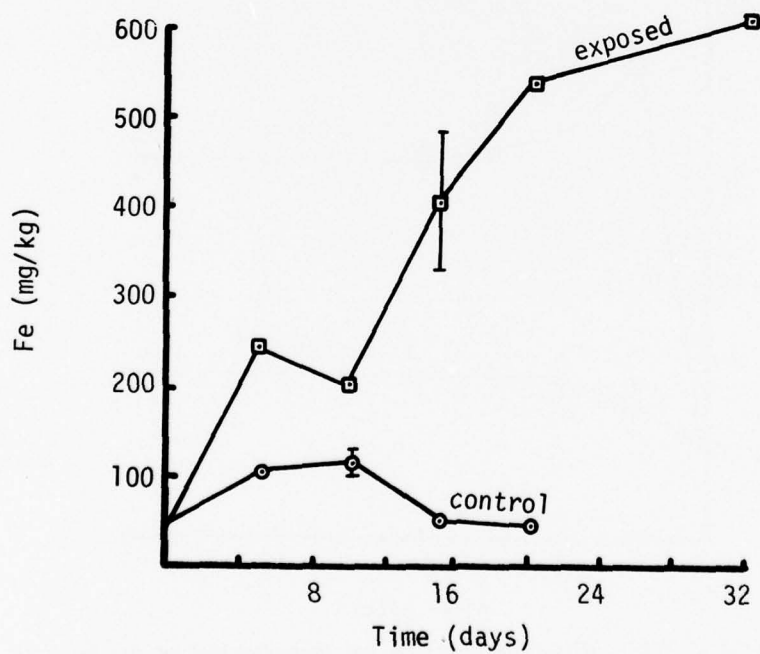


Figure 10. Mean Fe Uptake by *Palaemonetes kadiakensis* Exposed to Ashtabula Sediment in fresh water

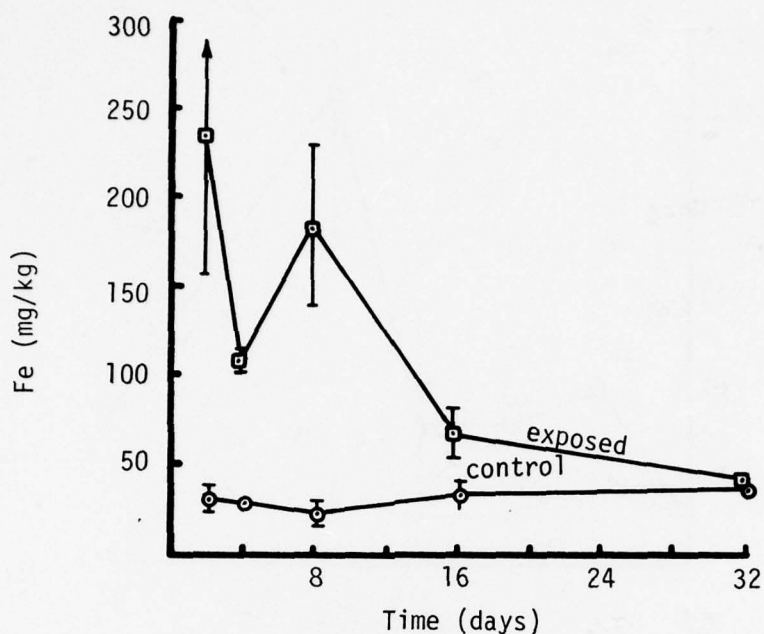


Figure 11. Mean Fe Uptake by *Palaemonetes pugio*
Exposed to Texas City Sediment at 15‰ S

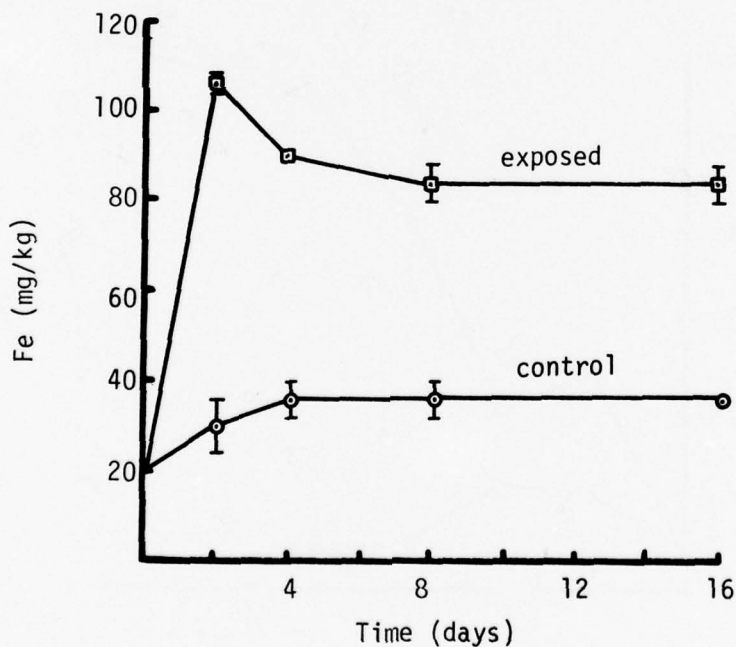


Figure 12. Mean Fe Uptake by *Palaemonetes pugio*
Exposed to Texas City Sediment at 30‰ S

respectively). Iron levels were lower at all subsequent sampling times. At 15‰S, tissue Fe concentrations dropped gradually to near the levels in control animals at day 32. At 30‰S, tissue Fe levels dropped only slightly from the day-2 peak to a mean of 84 mg/kg on days 8 and 16. However, at all sampling times, Fe levels were higher in sediment-exposed animals than in the controls.

73. Statistical analysis of the data from exposure of *P. pugio* to Corpus Christi sediment at 15‰S and 30‰S revealed that exposure alone contributed to Fe uptake and that this contribution was marginal ($P > F = 0.05$). Salinity, time, and the three first-order interactions were not significant. Analysis of variance tests performed separately on each exposure showed that accumulation was significant at 15‰S but not at 30‰S. At 15‰S, animals exposed to the sediment contained higher mean Fe levels than controls at all sampling times, with a maximum of 129 mg/kg being reached after 4 days exposure (Figure 13). At 30‰S, Fe levels were higher in exposed than in control shrimp at days 2 and 4, but not at day 8 (Figure 14).

74. Animals exposed at 15‰S to sediment for 8 days and then allowed to depurate for 8 days contained a mean of 45 mg/kg Fe compared to 82 mg/kg in the 8-day exposed animals. At 30‰S, the corresponding values were 26 mg/kg and 32 mg/kg, respectively.

75. *Neanthes arenaceodentata*. The polychaete worm *N. arenaceodentata* did not show significant accumulation of Fe during exposure to Texas City sediment at 30‰S. Mean tissue Fe concentrations of control and exposed animals showed considerable temporal variation and overlap

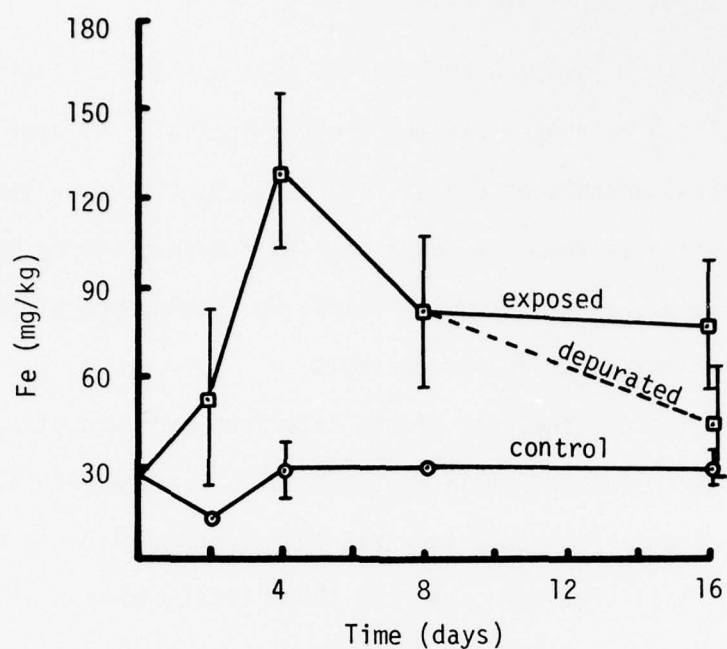


Figure 13. Mean Fe Uptake by *Palaemonetes pugio* Exposed to Corpus Christi Sediment at 15‰ S

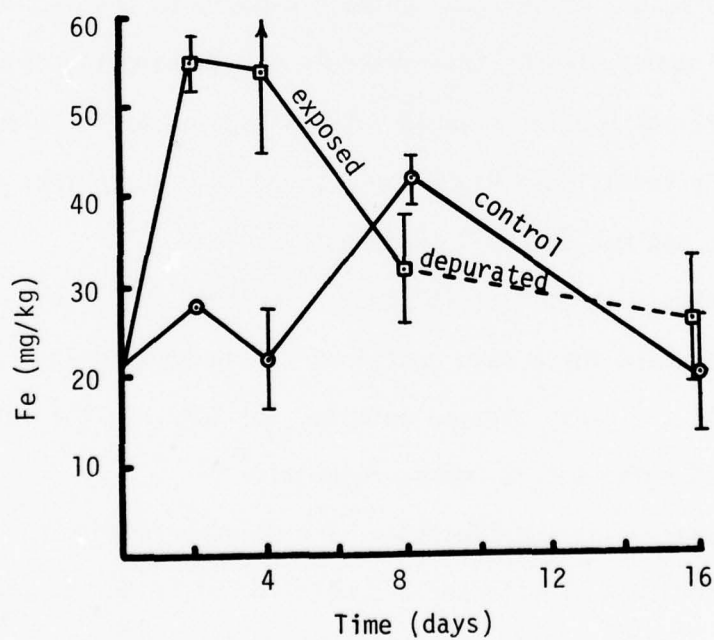


Figure 14. Mean Fe Uptake by *Palaemonetes pugio* Exposed to Corpus Christi Sediment at 30‰ S

during the course of the experiment (Figure 15). In the 8-day uptake-8-day depuration experiment, the 8-day depurated worms had a higher mean tissue Fe concentration than the 8-day and 32-day experimentals and controls.

76. *N. arenaceodentata* were exposed to Corpus Christi sediment at 30‰S in two separate experiments. In the first experiment, exposure, time, and their interaction all contributed significantly to the observed Fe uptake patterns. There was a somewhat cyclical pattern of Fe uptake by the sediment-exposed worms (Figure 16). This cyclic pattern was also shown in *N. arenaceodentata* for several other metals. Tissue Fe levels in exposed animals rose from 67 mg/kg at day 0 to 438 mg/kg at day 2. Tissue Fe concentrations then dropped to the 200 range at the subsequent three sampling times and finally rose again to 639 mg/kg at day 32. At all sampling times Fe concentrations were higher in exposed than in control worms.

77. In the second exposure to Corpus Christi sediment, the worms showed no significant accumulation of Fe. In this experiment, 0-day controls had a higher tissue Fe burden (119 mg/kg) than 0-day control worms in the previous exposure (76 mg/kg). This suggests a cyclical variation in the normal body burden of Fe in our laboratory population of *N. arenaceodentata*. There was little difference between control and experimental worms in tissue Fe levels at any sampling time (Figure 17). In worms allowed to depurate for 8 days, following 8 days exposure to the sediment, tissue Fe concentrations dropped from a mean of 121 mg/kg to 108 mg/kg.

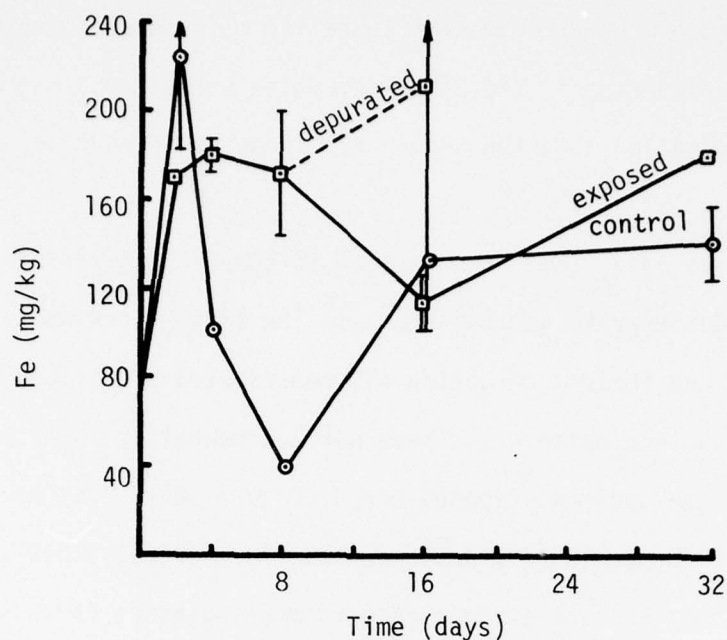


Figure 15. Mean Fe Uptake by *Neanthes arenaeodentata* Exposed to Texas City Sediment at 30‰S

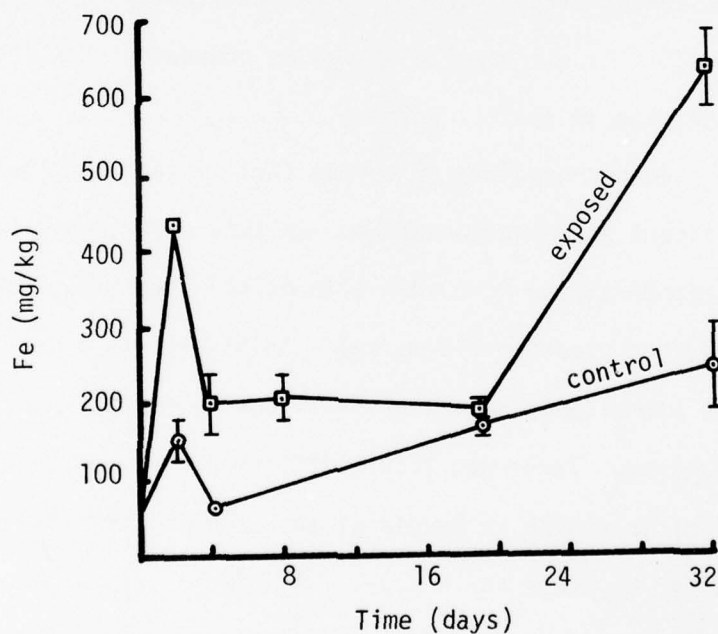


Figure 16. Mean Fe Uptake by *Neanthes arenaeodentata* Exposed to Corpus Christi Sediment at 30‰S [First Run]

78. *Tubifex* sp. The freshwater annelid *Tubifex* sp., like *N. arenaceodentata* in Corpus Christi sediment, showed a cyclic pattern of Fe accumulation during exposure to Ashtabula sediment in fresh water. Exposure, time, and their interaction all contributed significantly to the Fe uptake observed. The highest levels of tissue Fe in sediment-exposed worms were observed at day 2 (1550 mg/kg) and day 32 (1310 mg/kg) (Figure 18). Iron concentrations in control worms varied from 440 mg/kg to 913 mg/kg and showed a definite rising trend during the course of the experiment.

79. A group of worms was exposed to the sediment for 8 days and then sampled after 2 days and 8 days of depuration. Tissue Fe levels were 1034 mg/kg and 887 mg/kg after 2 days and 8 days of depuration, respectively, compared to 660 mg/kg before depuration commenced.

Manganese (Mn)

80. Statistical analyses of Mn accumulation by all species are summarized in Table A2.

81. *Rangia cuneata*. Clams *R. cuneata* were exposed to Texas City sediment at both 15‰ and 30‰. The concentration of Mn in the clams was significantly affected by exposure, salinity, and interaction of exposure and time. Animals exposed to sediment at 30‰ had higher mean tissue Mn concentrations than controls at all but the day 16 sampling time (Figure 19). At 15‰, Mn levels in tissues of sediment-exposed clams rose to 31 mg/kg at day 4, leveled off until day 8, and then declined and stabilized at a lower level on days 16 and 32 (Figure 20). Control animals showed an almost parallel pattern of initial

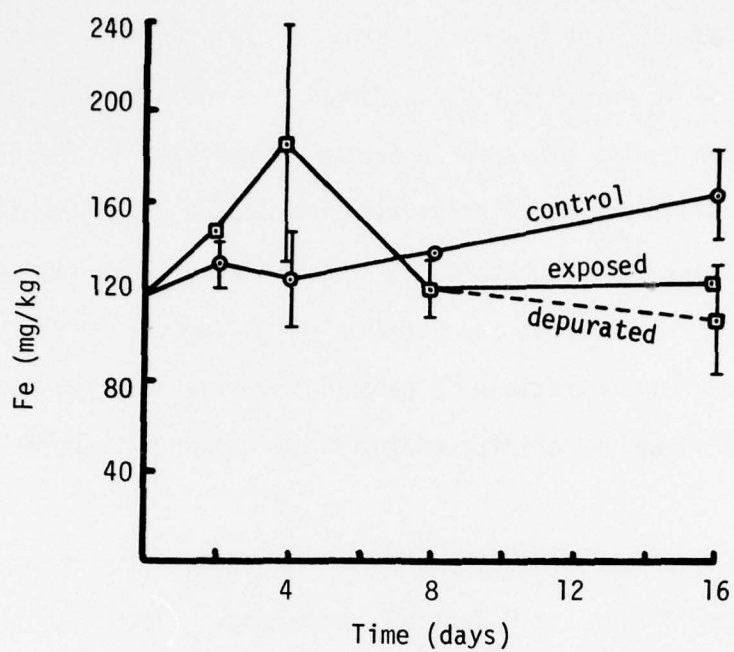


Figure 17. Mean Fe Uptake by *Neanthes arenaeodentata* Exposed to Corpus Christi Sediment at 30‰ S [Second Run]

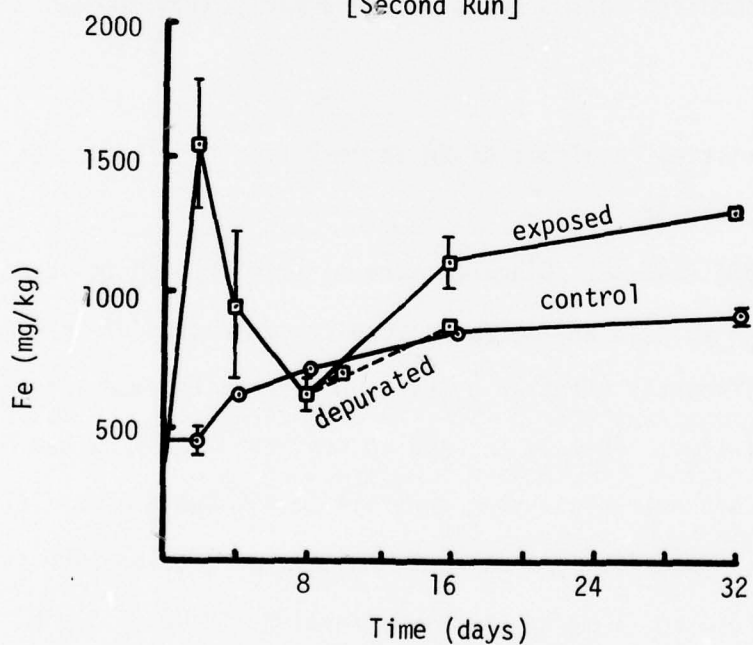


Figure 18. Mean Fe Uptake by *Tubifex* sp. Exposed to Ashtabula Sediment in fresh water

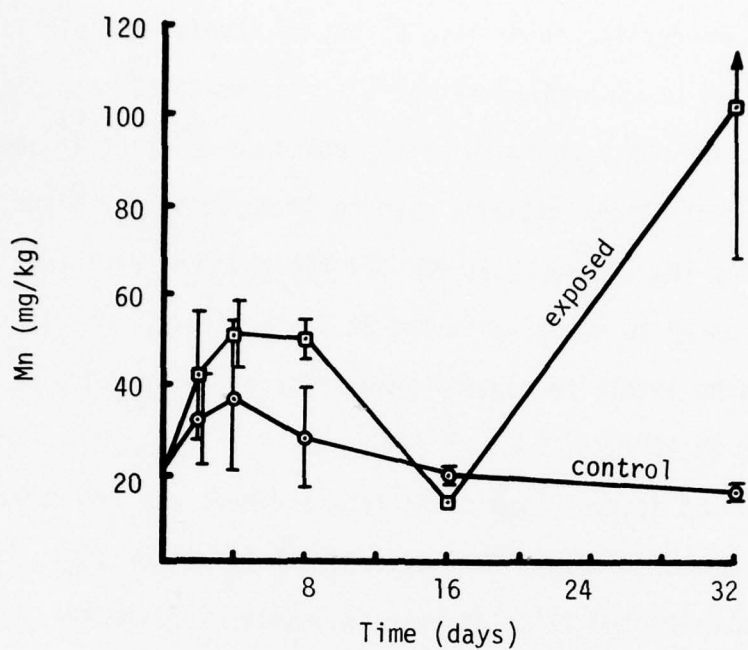


Figure 19. Mean Mn Uptake by *Rangia cuneata*
Exposed to Texas City Sediment at 30‰ S

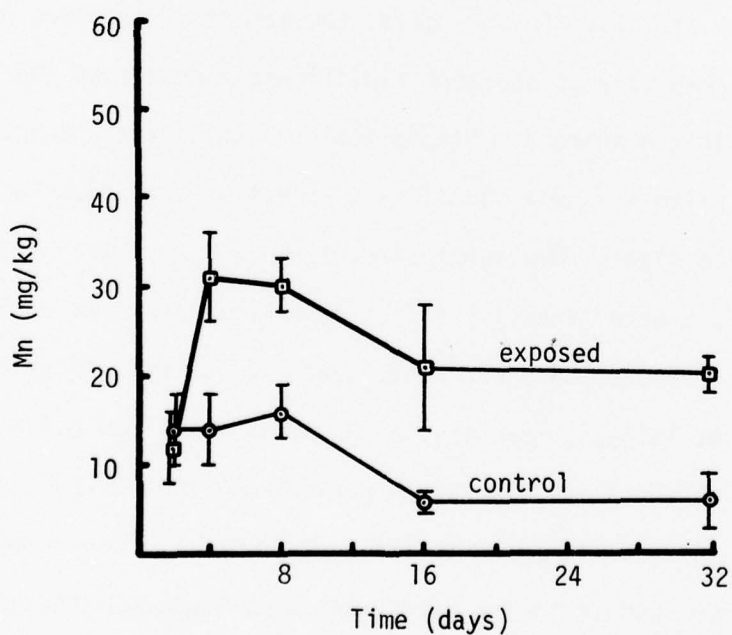


Figure 20. Mean Mn Uptake by *Rangia cuneata*
Exposed to Texas City Sediment at 30‰ S

increase and then decline in Mn levels, but Mn levels in controls were lower than those in exposed animals at all but the day 2 sampling time. A similar pattern was seen in animals exposed to sediment at 30‰. Tissue Mn concentrations initially rose to 51 mg/kg at day 4 and then declined on day 16. However, at day 32, the mean Mn level rose to 102 mg/kg compared to 16 mg/kg in the 32 day controls. At all sampling times, tissue Mn levels in control animals were nearly twice as high at 30‰ as at 15‰.

82. No net accumulation of Mn from sediment was demonstrated in *R. cuneata* exposed to Corpus Christi sediment at either 15‰ or 30‰ (Figures 21 and 22). At both salinities, sediment-exposed animals had lower tissue Mn levels than controls at all sampling times, suggesting that this sediment was serving as a sink rather than a source of Mn to these animals. In this case, the effect of exposure was inverse (i.e. exposure to sediment significantly decreased the bioavailability of Mn to the animal). Statistical analysis revealed that both exposure and salinity had a significant effect on the levels of Mn measured in the clams. Manganese concentrations in control and exposed clams at 30‰ were generally higher than those in clams at 15‰.

83. The depuration experiments gave similar results at both salinities. At 15‰, mean tissue Mn levels rose from 8.2 mg/kg to 14 mg/kg during the 8 day depuration period, while at 30‰, levels rose from 10 mg/kg to 16 mg/kg in the same period. These results provide further support to the hypothesis that sediments decreased the bioavailability of Mn to clams.

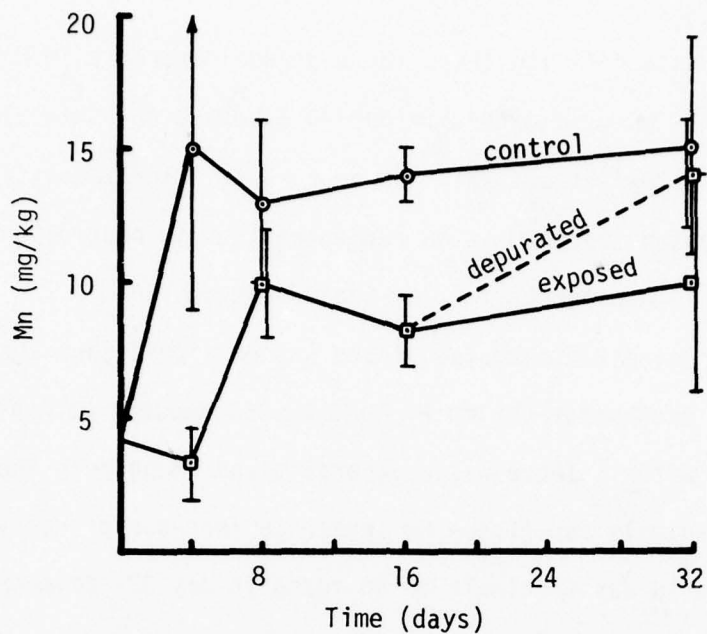


Figure 21. Mean Mn Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 15‰S

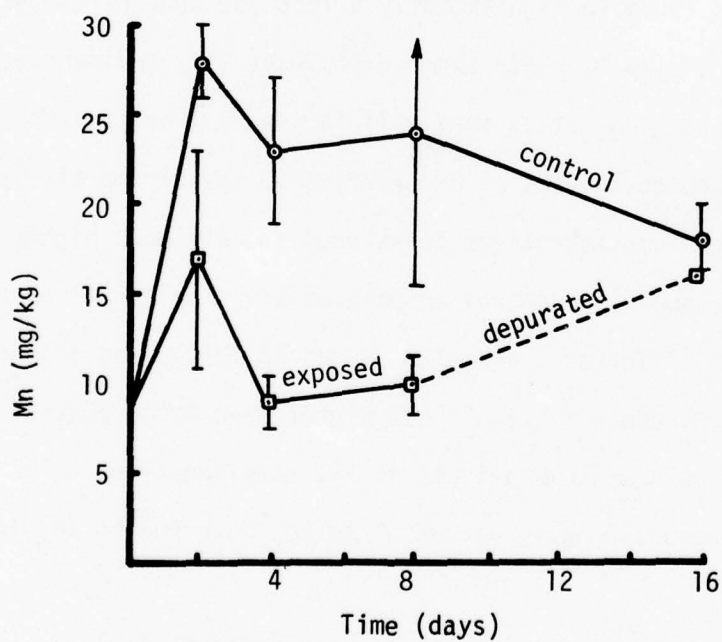


Figure 22. Mean Mn Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 30‰S

84. There was a definite trend for a gradual increase in Mn levels in the tissues of *R. cuneata* with time during exposure to Ashtabula sediment in fresh water (Figure 23). However, statistical analysis indicated no significant difference in Mn concentrations in control and exposed clams due to exposure, time, or their interaction.

85. *Palaemonetes kadiakensis*. There was no significant accumulation of Mn by the freshwater shrimp *P. kadiakensis* exposed to Ashtabula sediment in fresh water. There was a general trend among both the control and exposed animals for tissue Mn levels to increase gradually with time from 17 mg/kg in day 0 animals to 40 mg/kg in day 32 sediment-exposed animals (Figure 24).

86. *Palaemonetes pugio*. Salinity and the interaction of exposure and salinity were found to significantly affect the concentration of Mn in the estuarine shrimp *P. pugio* exposed to Texas City sediment at 15‰ and 30‰, indicating that salinity had a greater effect than exposure on the concentrations of Mn observed in the shrimp tissues. At 15‰, mean Mn concentrations in exposed animals were higher than those in the corresponding control animals at all sampling times (Figure 25). The largest difference, 45 mg/kg versus 23 mg/kg, was recorded on day 8. At 30‰, control animals had higher mean Mn concentrations than the corresponding exposed animals at all sampling times. The largest differences, 150 mg/kg versus 51 mg/kg, occurred on day 4 (Figure 26).

87. *P. pugio* exposed to Corpus Christi sediment at 15‰ and 30‰ did not show a significant accumulation of Mn due to exposure,

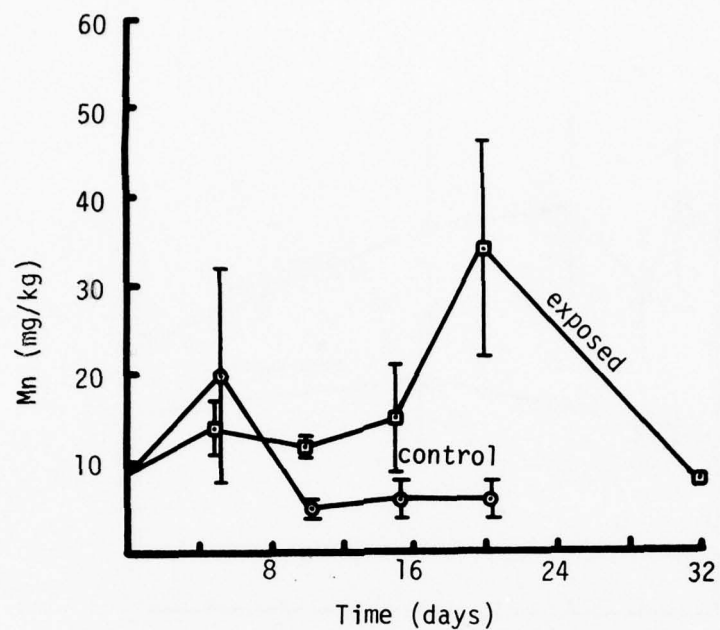


Figure 23. Mean Mn Uptake by *Rangia cuneata* Exposed to Ashtabula Sediment in fresh water

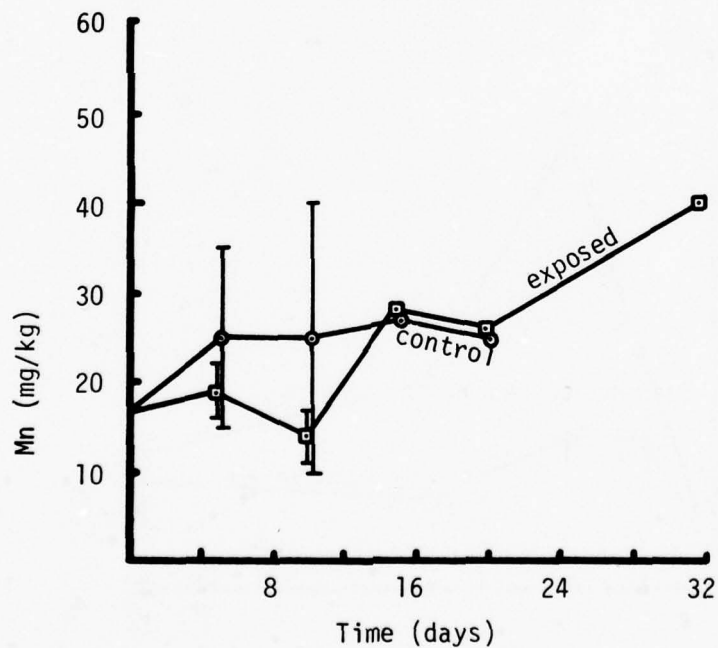


Figure 24. Mean Mn Uptake by *Palaemonetes kadiakensis* Exposed to Ashtabula Sediment in fresh water

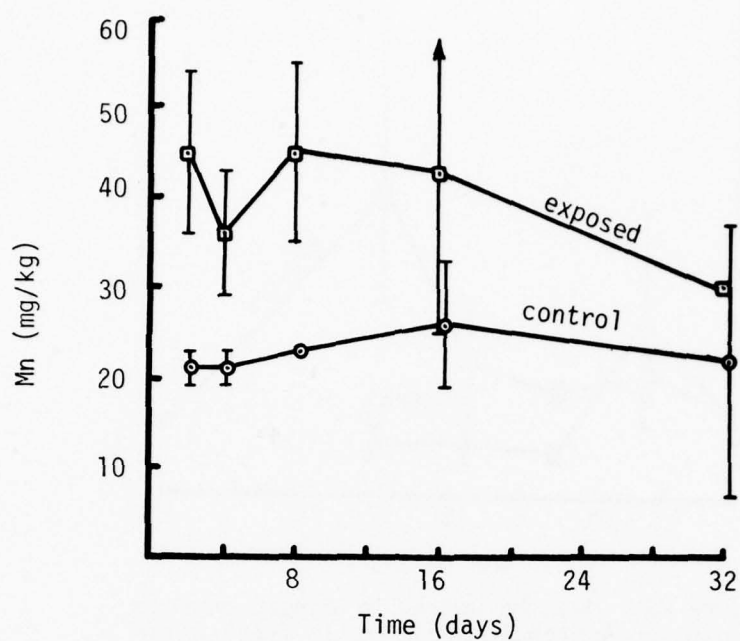


Figure 25. Mean Mn Uptake by *Palaemonetes pugio*
Exposed to Texas City Sediment at 15‰S

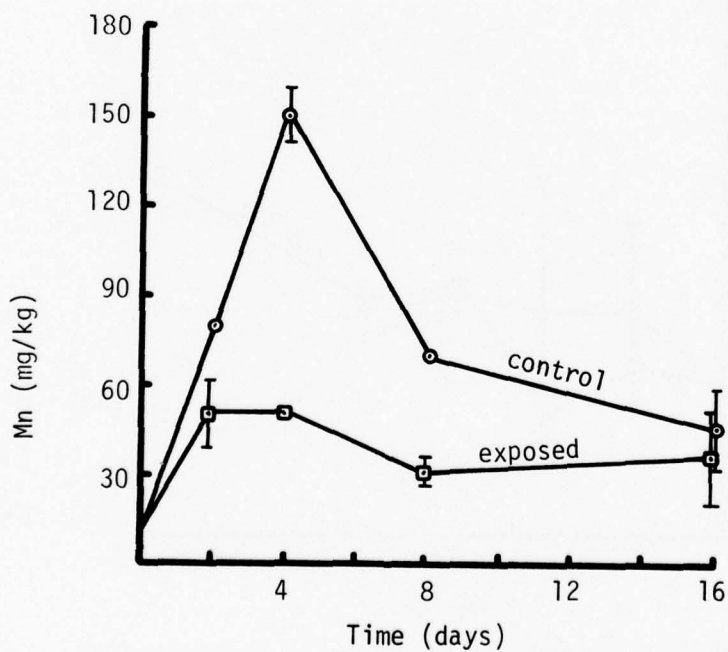


Figure 26. Mean Mn Uptake by *Palaemonetes pugio*
Exposed to Texas City Sediment at 30‰S

salinity, temperature, or their interactions. At 15‰, Mn concentrations in the sediment-exposed shrimp rose from 19 mg/kg on day 2 to 50 mg/kg on day 16. However, mean concentrations in the control shrimp also varied between 19 mg/kg and 49 mg/kg (Figure 27). At 30‰, Mn levels in the exposed shrimp were lower than the corresponding values in control shrimp at all sampling times (Figure 28). In animals exposed to the sediment for 8 days and then allowed to depurate for 8 days in sediment free seawater, tissue Mn levels dropped slightly from 25 mg/kg to 22 mg/kg at 15‰; but at 30‰, Mn levels rose from 22 mg/kg to 52 mg/kg, while Mn levels in controls dropped from 46 mg/kg to 21 mg/kg during the same time period. These results suggest that, at 30‰ but not at 15‰, the presence of Corpus Christi sediment decreased the bioavailability of Mn to *P. pugio*.

88. *Neanthes arenaceodentata*. The worm *N. arenaceodentata* exposed to Texas City sediment at 30‰ did not show significant accumulation of Mn. At most sampling times Mn concentrations were similar in the control and exposed worms (Figure 29). The exceptions occurred at day 2 when the control animals contained a mean of 40 mg/kg Mn compared to 27 mg/kg in the exposed worms, and at day 32 when the values were 10 mg/kg and 20 mg/kg in the control and exposed animals, respectively. The Mn concentration dropped from 24 mg/kg to 16 mg/kg in animals exposed to sediment for 8 days and then allowed to depurate for an additional 8 days.

89. In two separate experiments, *N. arenaceodentata* exposed to Corpus Christi sediment at 30‰ failed to show significant accumula-

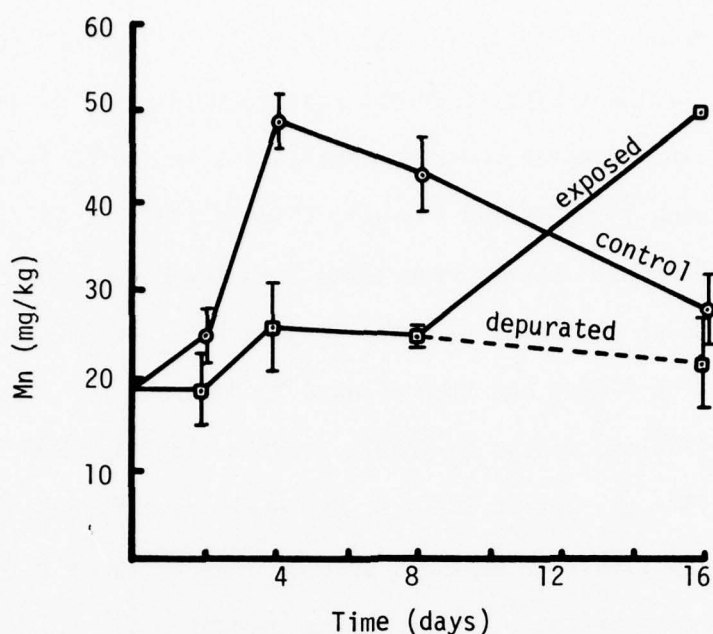


Figure 27. Mean Mn Uptake by *Palaemonetes pugio*
Exposed to Corpus Christi Sediment at 15‰S

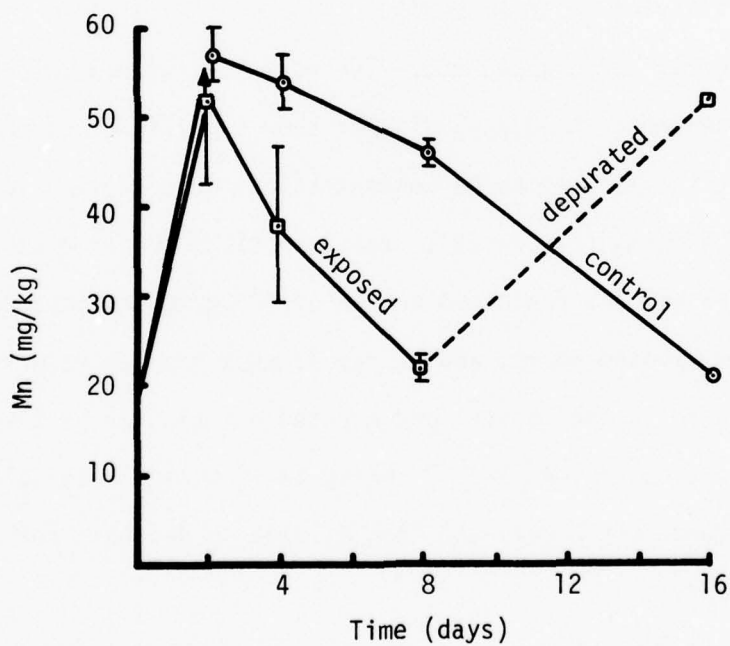


Figure 28. Mean Mn Uptake by *Palaemonetes pugio*
Exposed to Corpus Christi Sediment at 30‰S

tion of Mn. In the first experiment, the sediment-exposed worms contained higher mean Mn levels than the corresponding controls at all sampling times (Figure 30). The largest difference occurred at the day 32 sampling time when mean concentrations of 20 mg/kg and 92 mg/kg were measured in the control and exposed worms, respectively. The probability of a larger F factor ($P > F$) due to exposure was 0.06 indicating marginal significance. In the second experiment, mean Mn levels in control and exposed animals were similar at all sampling times and varied from 14 mg/kg to 22 mg/kg (Figure 31). In the second experiment, mean tissue Mn concentrations rose from 20 mg/kg to 30 mg/kg during 8 days depuration following 8 days exposure to the sediment.

90. *Tubifex* sp. The freshwater annelid *Tubifex* sp. failed to accumulate significant amounts of Mn from Ashtabula sediment in fresh water. Mean Mn levels in exposed and control worms were similar and varied from 9 mg/kg to 26 mg/kg at all sampling times except on day 2 when sediment-exposed animals contained 37 mg/kg (Figure 32). The uptake-depuration experiment showed no evidence of change in tissue Mn concentration after 2 days or 8 days of depuration.

Copper (Cu)

91. Statistical analyses of Cu accumulation by all species are summarized in Table A3.

92. *Rangia cuneata*. Copper was not accumulated from Texas City sediment at either 15‰ or 30‰ by the clam *R. cuneata*. Although exposure, time, and their interaction were without significant effect on Cu uptake, salinity was found to have a significant effect ($P > F = 0.02$)

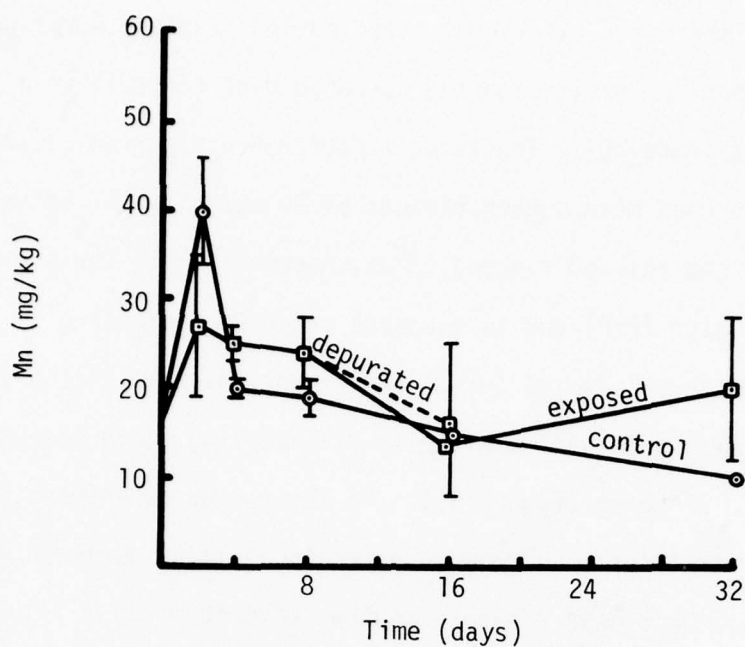


Figure 29. Mean Mn Uptake by *Neanthes arenaeodentata* Exposed to Texas City Sediment at 30‰S

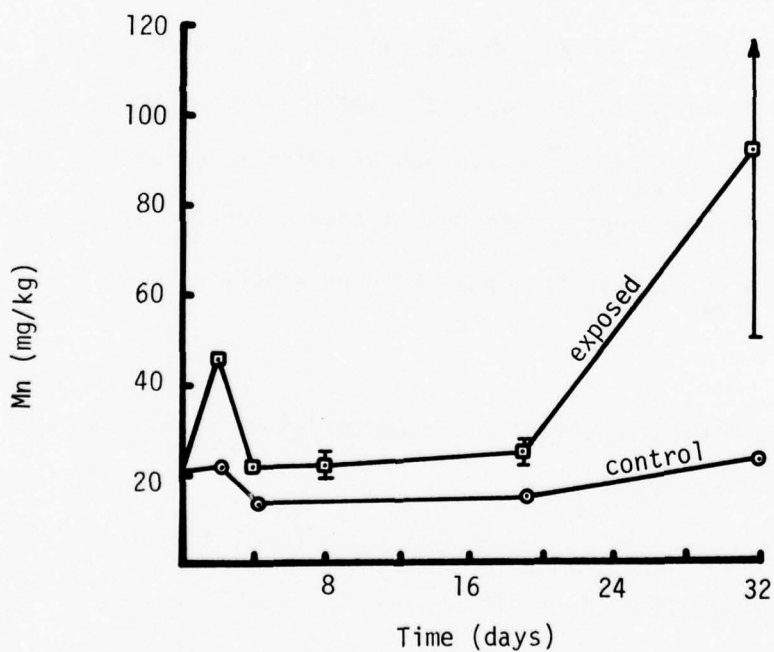


Figure 30. Mean Mn Uptake by *Neanthes arenaeodentata* Exposed to Corpus Christi Sediment at 30‰S [First Run]

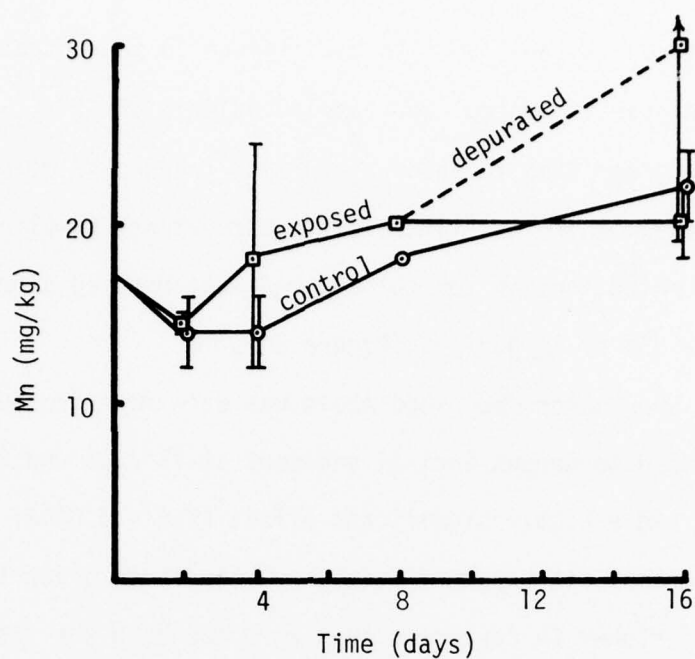


Figure 31. Mean Mn Uptake by *Neanthes arenaeodentata* Exposed to Corpus Christi Sediment at 30‰S [Second Run]

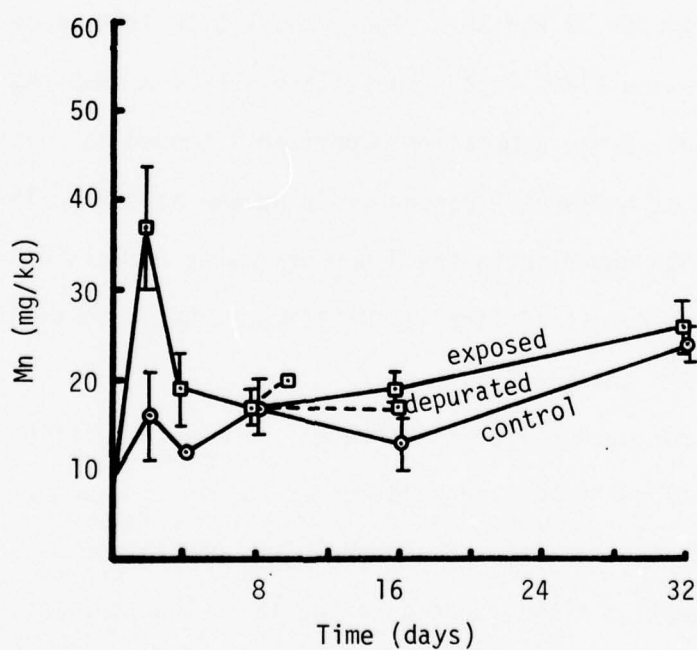


Figure 32. Mean Mn Uptake by *Tubifex* sp. Exposed to Ashtabula Sediment in fresh water

on the levels of Cu in the clam tissues. Tissue Cu concentrations were significantly higher in control and exposed animals at 15‰ (range, 18 mg/kg to 39 mg/kg) than in those at 30‰ (range, 12 mg/kg to 19 mg/kg). However there was little difference at any sampling time between Cu concentrations in control and sediment-exposed clams at 15‰ (Figure 33) or at 30‰ (Figure 34).

93. The phenomenon described above was even more pronounced for *R. cuneata* exposed to Corpus Christi sediment at 15‰ and 30‰. Again salinity had a highly significant effect ($P > F = 0.0004$) on Cu levels in the clams, but exposure, time, and the first order interactions did not. Higher Cu concentrations were found in the tissues of control and exposed animals at 15‰ (range of means, 15 mg/kg to 27 mg/kg) than in those at 30‰ (range of means, 7.0 mg/kg to 10.1 mg/kg) (Figures 35 and 36). There was little difference between control and exposed clams in tissue Cu levels at any sampling time. The 8-day uptake, 8-day depuration experiments tended to support the lack of effect of sediment exposure on Cu uptake at either 15‰ or 30‰. In both experiments the 8-day depurated animals had slightly higher, although not statistically significant, Cu concentrations than the 8-day exposed animals.

94. *R. cuneata* exposed to Ashtabula sediment in fresh water also failed to show significant accumulation of Cu due to exposure or time. Generally, both the control and exposed clams had tissue Cu concentrations in the same range as clams exposed to the above two sediments at 15‰. However, at day 20, sediment-exposed clams contained a mean of 40 mg/kg

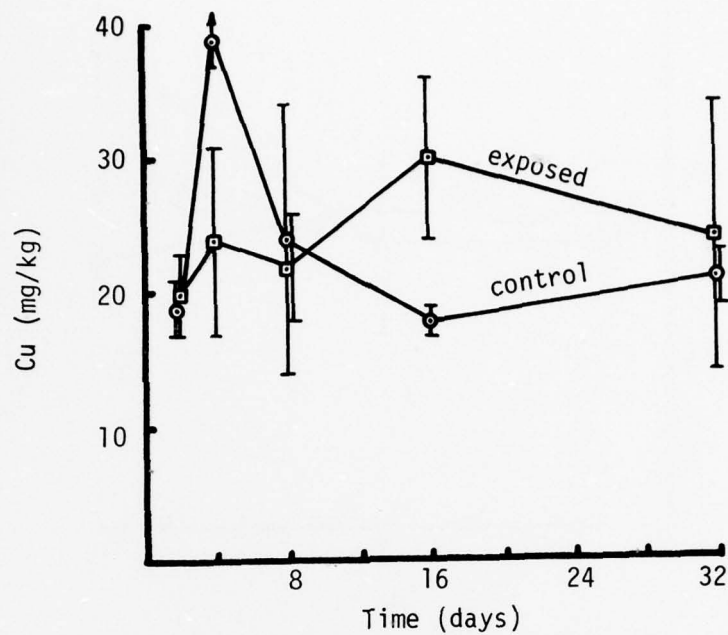


Figure 33. Mean Cu Uptake by *Rangia cuneata*
Exposed to Texas City Sediment at 15‰S

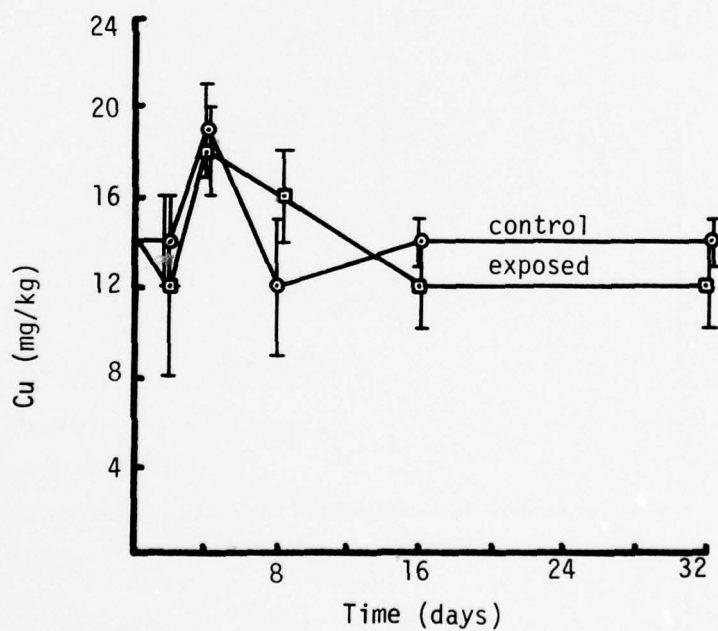


Figure 34. Mean Cu Uptake by *Rangia cuneata*
Exposed to Texas City Sediment at 30‰S

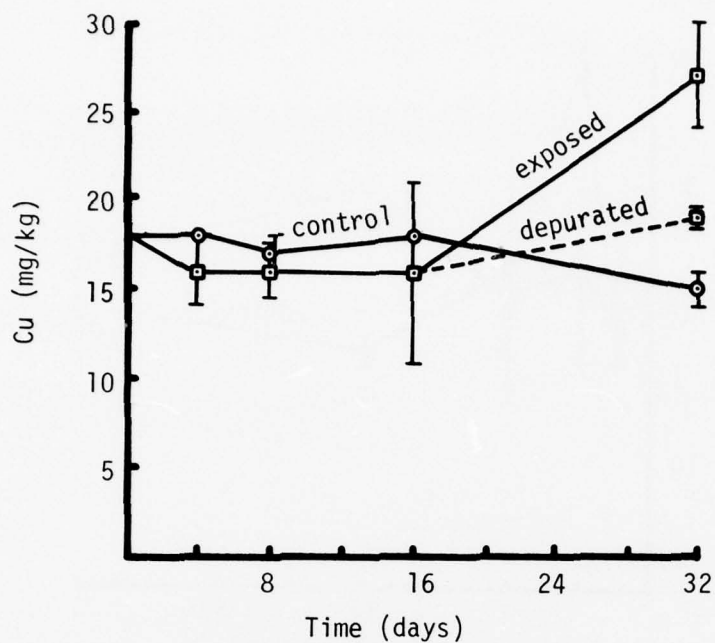


Figure 35. Mean Cu Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 15‰S

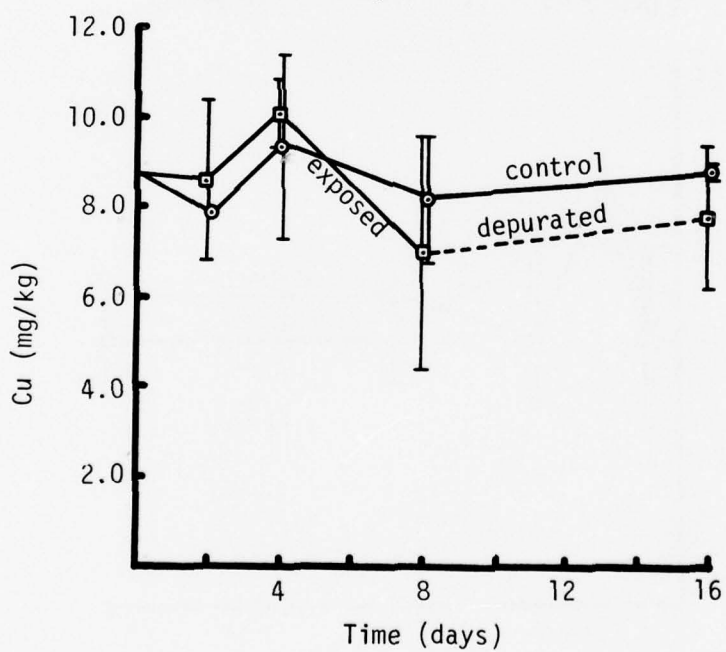


Figure 36. Mean Cu Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 30‰S

Cu (Figure 37). Thus, there seemed to be a definite trend toward increasing body burdens of Cu with decreasing salinity.

95. *Palaemonetes pugio* and *P. kadiakensis*. The two shrimp investigated, *P. pugio* and *P. kadiakensis*, contained high, but relatively stable, concentrations of Cu (range of means, 54 mg/kg to 180 mg/kg Cu). This is not unexpected, since these crustaceans possess the Cu-containing respiratory pigment, hemocyanin. The general patterns of tissue Cu distribution were similar for both species, for the 3 sediments, and for the 3 salinities. With few exceptions, Cu concentrations in the control animals were higher than those in the sediment-exposed animals at each sampling time in all 5 exposure experiments (Figures 38-42). In each experiment, there was a definite trend for Cu concentration to increase with time in both the control and exposed groups. However, with one exception, the Cu concentration in the animals was not significantly affected by exposure, time, salinity, or their interactions. Salinity had a significant effect on Cu concentrations in *P. pugio* exposed to Corpus Christi sediment. In the uptake:depuration experiments conducted with *P. pugio* exposed to Corpus Christi sediments at 15‰ and 30‰, Cu levels were lower in animals exposed to sediments for 8 days than in those exposed for 8 days and then allowed to depurate for 8 days.

96. *Neanthes arenaceodentata* exposed to Texas City sediment at 30‰ showed a significant accumulation of Cu. There appeared to be a cyclic variation in Cu concentrations, particularly among the sediment-exposed worms (Figure 43). Thus, the effect of time on tissue Cu was found to be non-significant.

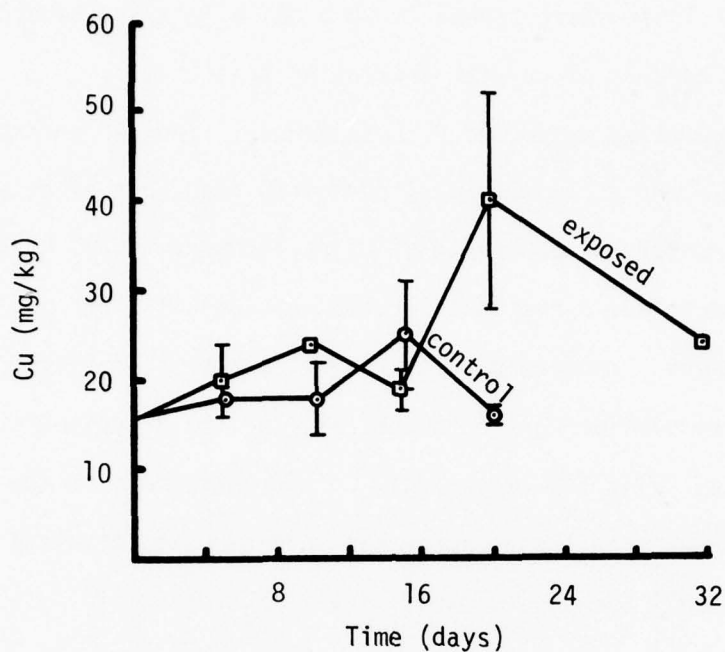


Figure 37. Mean Cu Uptake by *Rangia cuneata* Exposed to Ashtabula Sediment in fresh water

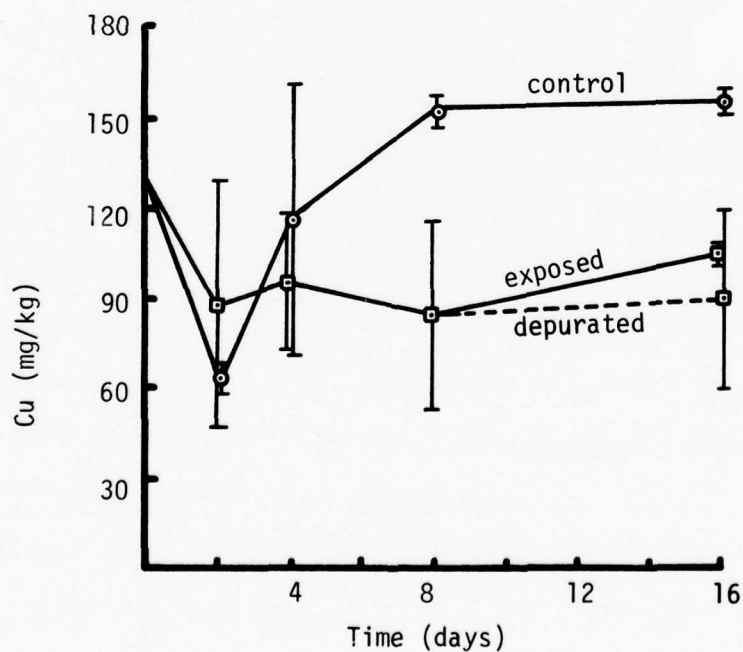


Figure 38. Mean Cu Uptake by *Palaemonetes pugio* Exposed to Corpus Christi Sediment at 15‰S

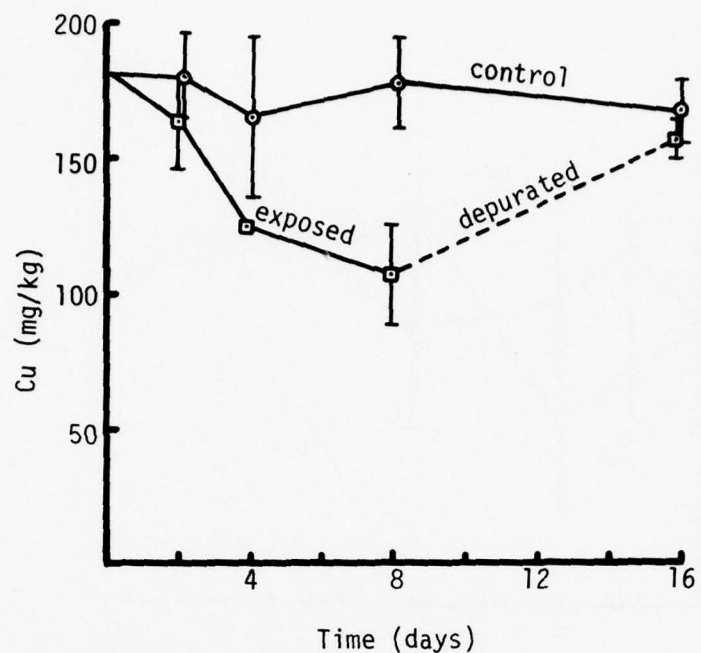


Figure 39. Mean Cu Uptake by *Palaemonetes pugio* Exposed to Corpus Christi Sediment at 30‰ S

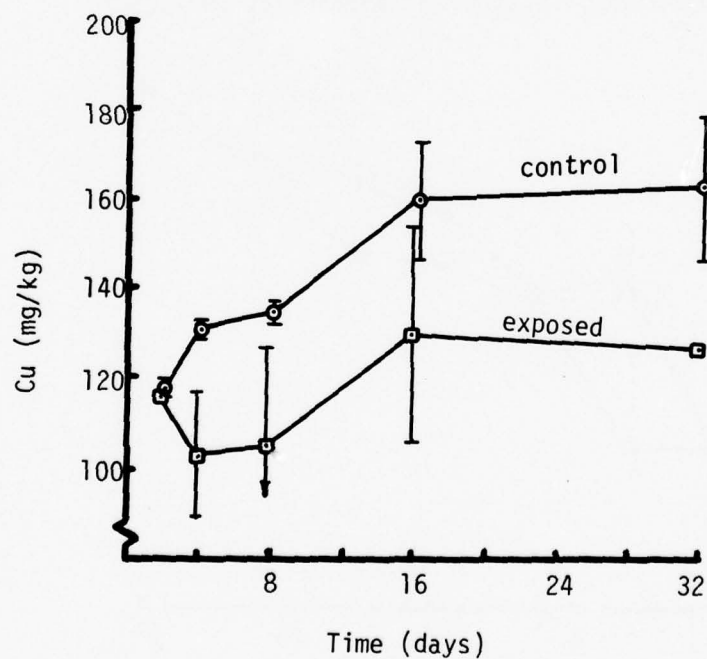


Figure 40. Mean Cu Uptake by *Palaemonetes pugio* Exposed to Texas City Sediment at 15‰ S

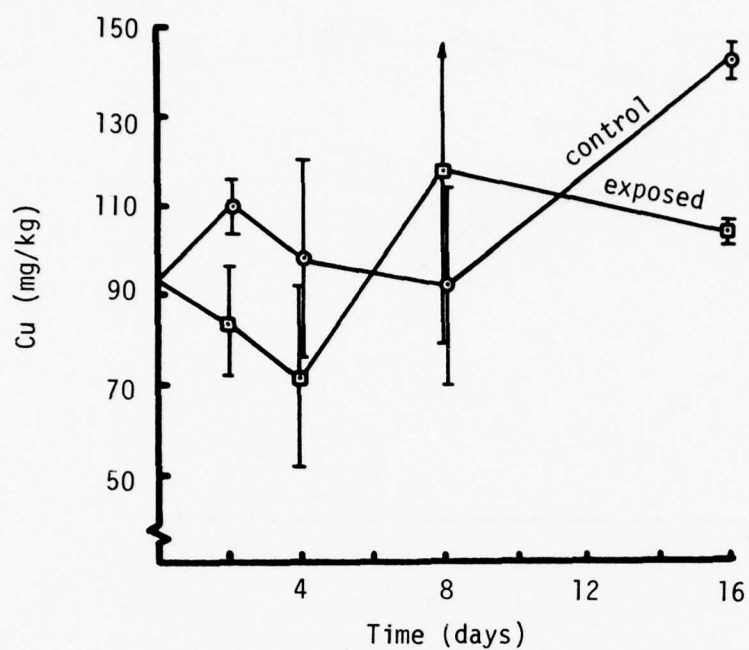


Figure 41. Mean Cu Uptake by *Palaemonetes pugio*
Exposed to Texas City Sediment at 30‰S

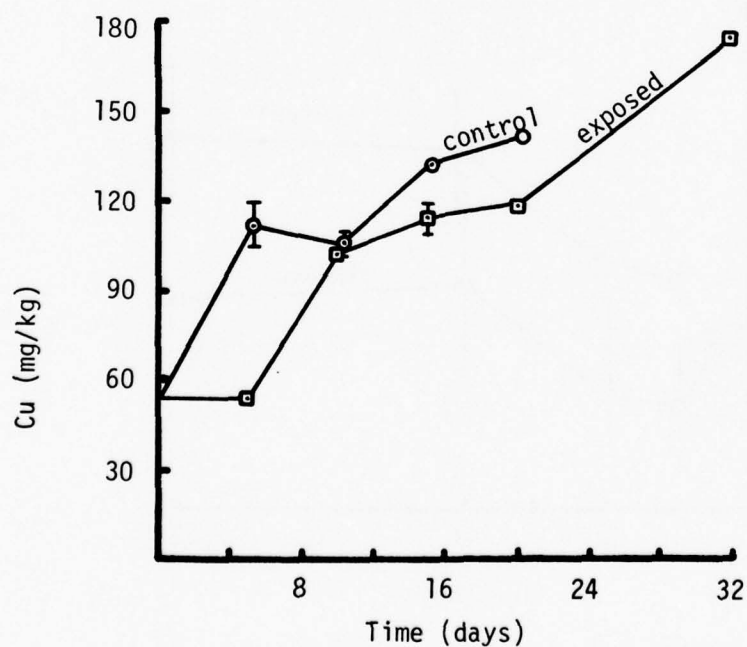


Figure 42. Mean Cu Uptake by *Palaemonetes kadiakensis*
Exposed to Ashtabula Sediment in fresh water

97. The two exposures of *N. arenaceodentata* to Corpus Christi sediment at 30‰ yielded different results. In the first exposure, Cu uptake was significantly affected by exposure, time, and their interaction. In the sediment-exposed worms, Cu concentrations rose from 38 mg/kg at day 2 to 92 mg/kg at day 32. Copper concentrations in the controls fluctuated between 27 mg/kg and 40 mg/kg (Figure 44).

98. In the second experiment, the worms did not accumulate significant amounts of Cu from the sediment. Copper concentrations were similar in the control and exposed worms at most sampling times and varied between 56 mg/kg and 74 mg/kg (Figure 45).

99. *Tubifex* sp. exposed to Ashtabula sediment in fresh water showed little variation in tissue Cu concentrations and no significant accumulation of this metal from the sediment. Copper concentrations in control worms varied even less, from 12 mg/kg to 16 mg/kg (Figure 46). There was also little variation in tissue Cu levels in the uptake-depuration experiment.

Cadmium (Cd)

100. Statistical analyses of Cd accumulation by all species are summarized in Table A4.

101. *Rangia cuneata*. Exposure to Texas City sediment at 15‰ and 30‰ did not have a significant effect on Cd accumulation by the clam *R. cuneata*. However, salinity had a highly significant effect on the levels of Cd measured in the clam tissues. At 15‰, the clams contained Cd residues in the range of 3 mg/kg to 5.8 mg/kg, while at 30‰, the range was 0.8 mg/kg to 1.1 mg/kg (Figures 47 and 48). At

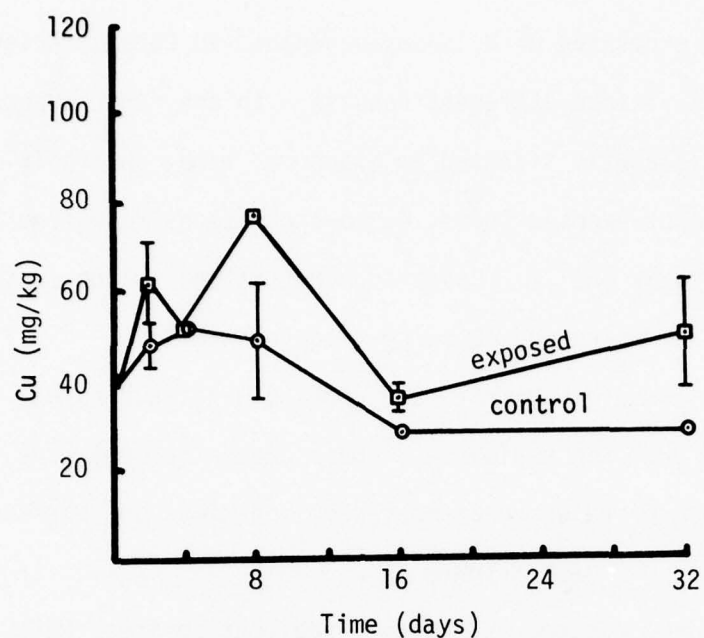


Figure 43. Mean Cu Uptake by *Neanthes arenaeodentata* Exposed to Texas City Sediment at 30‰ S

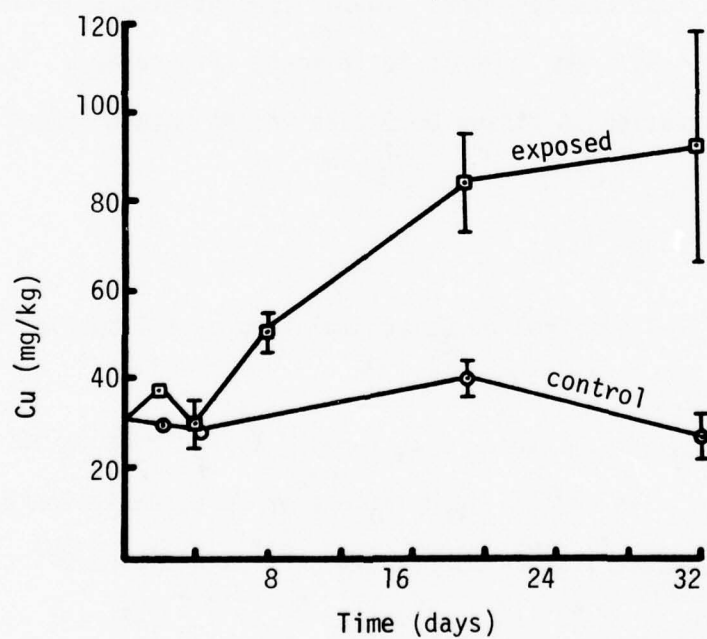


Figure 44. Mean Cu Uptake by *Neanthes arenaeodentata* Exposed to Corpus Christi Sediment at 30‰ S [First Run]

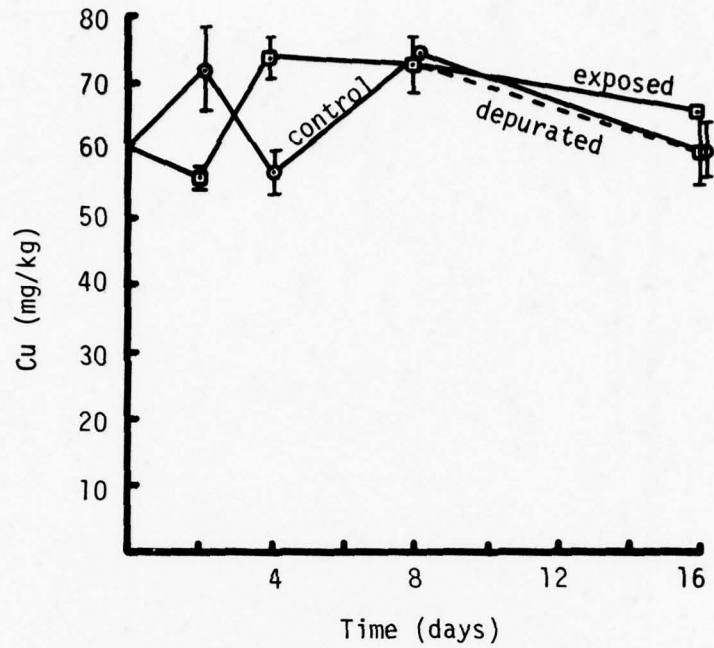


Figure 45. Mean Cu Uptake by *Neanthes arenaeodentata* Exposed to Corpus Christi Sediment at 30‰ S [Second Run]

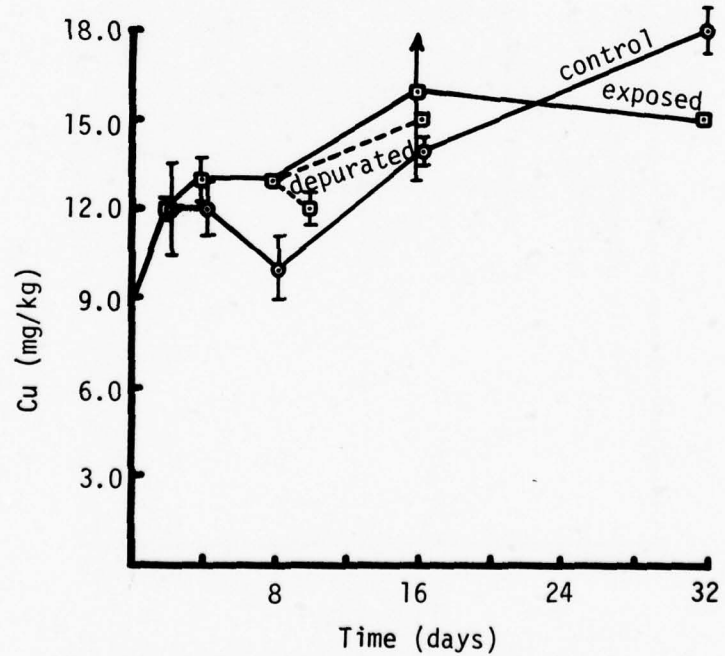


Figure 46. Mean Cu Uptake by *Tubifex* sp. Exposed to Ashtabula Sediment in fresh water

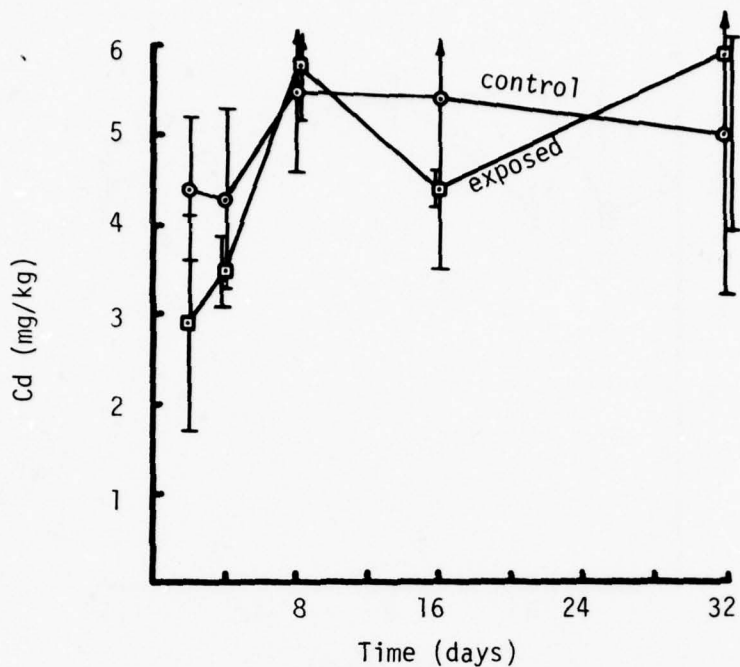


Figure 47. Mean Cd Uptake by *Rangia cuneata* Exposed to Texas City Sediment at 15‰S

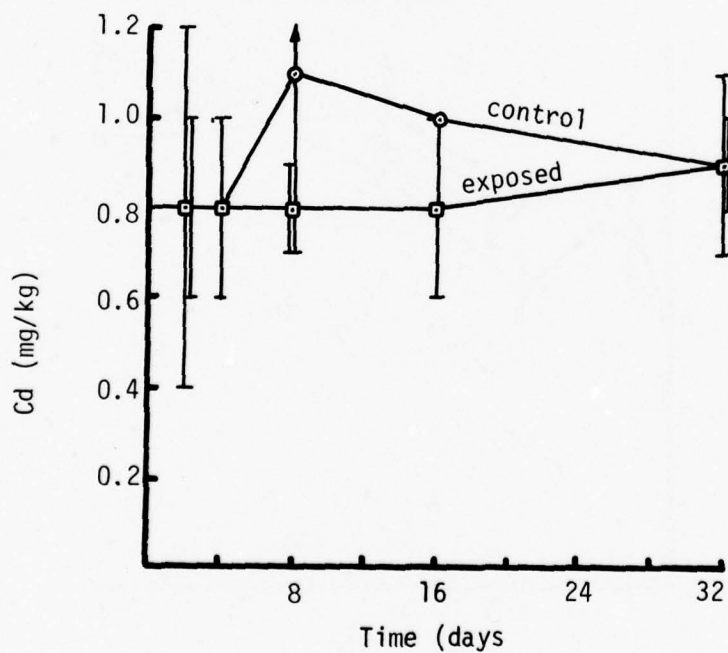


Figure 48. Mean Cd Uptake by *Rangia cuneata* Exposed to Texas City Sediment at 30‰S

each salinity, there was little difference in the Cd concentrations in controls and sediment-exposed animals.

102. *R. cuneata* exposed to Corpus Christi sediment at 15‰ and 30‰ showed a similar trend. Exposure, time, and the first-order interactions were without significant effect on the levels of tissue Cd measured, but salinity had a significant effect on Cd concentrations. However, in this case, clams exposed at 30‰ had higher mean tissue Cd levels (0.2 mg/kg to 0.5 mg/kg) than those exposed at 15‰ (0.12 mg/kg to 0.35 mg/kg) (Figures 49 and 50). There was relatively little difference in Cd levels between control and exposed animals at either salinity. In the depuration experiments, carried out on groups of clams following 8 days exposure to the sediment at the two salinities, there was a small drop in tissue Cd concentrations following 8 days depuration.

103. Cadmium concentrations in the tissues of control *R. cuneata* and those exposed to Ashtabula sediment in fresh water were similar at all sampling times (Figure 51). Tissue Cd concentrations varied from 1.1 mg/kg to 2.3 mg/kg. Exposure to the sediment was without significant effect on the patterns of Cd distribution observed.

104. *Palaemonetes pugio* exposed to Texas City sediment at 15‰ and 30‰ contained lower concentrations of Cd at all sampling times than did the unexposed controls (Figures 52 and 53). The difference in Cd levels between control and exposed shrimp was significant, suggesting that Cd accumulation was mainly via the water and that the presence of sediment rendered the Cd less available to the animals at both 15‰ and 30‰.

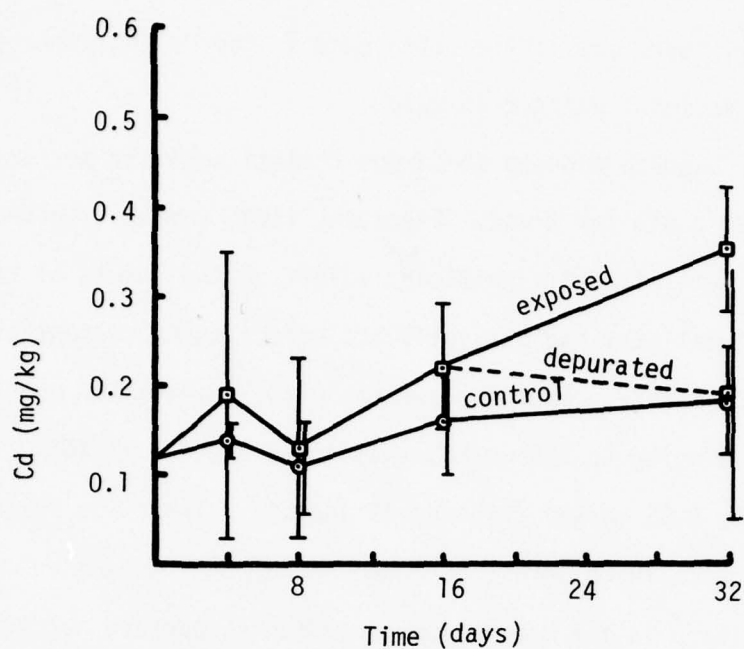


Figure 49. Mean Cd Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 15‰S

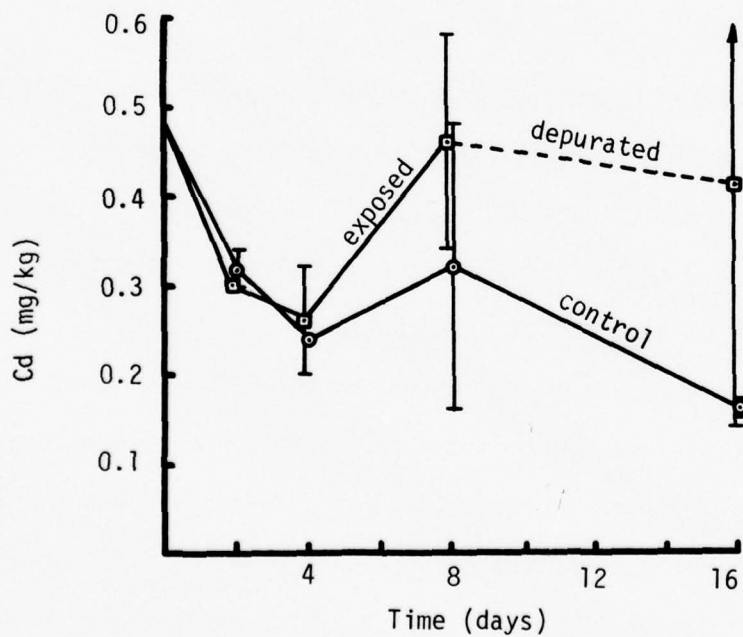


Figure 50. Mean Cd Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 30‰S

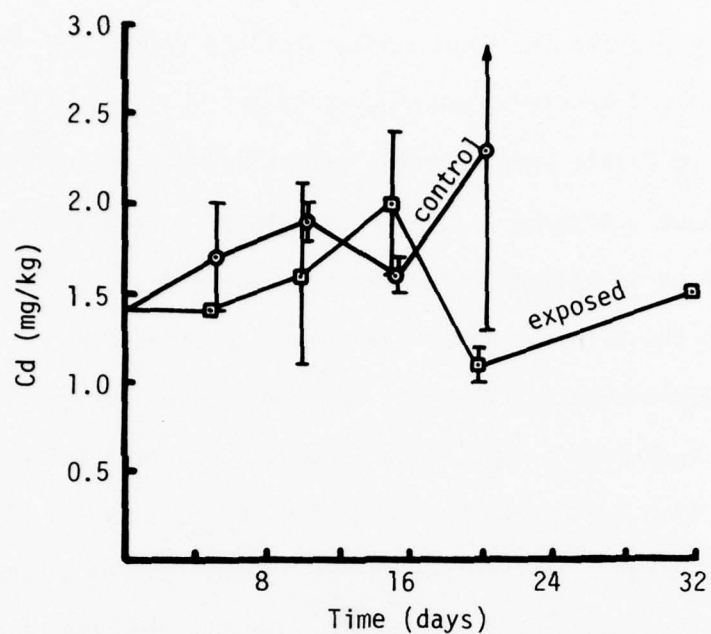


Figure 51. Mean Cd Uptake by *Rangia cuneata* Exposed to Ashtabula Sediment in fresh water

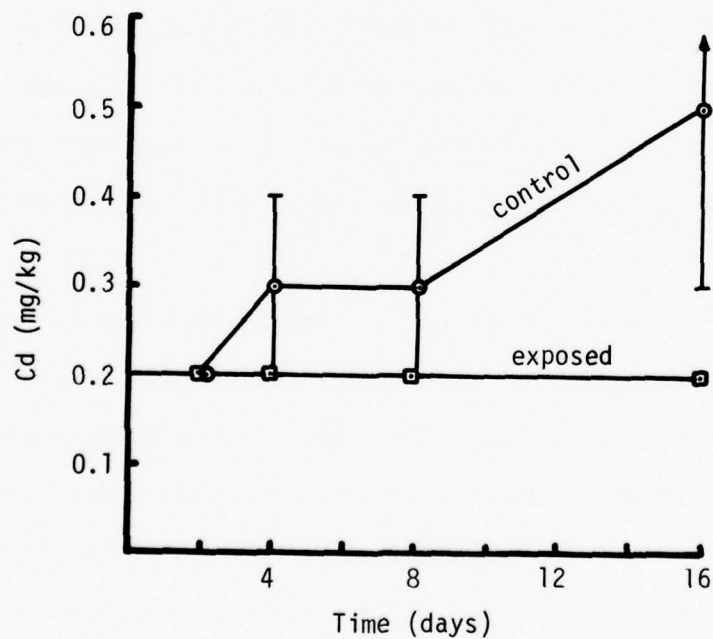


Figure 52. Mean Cd Uptake by *Palaemonetes pugio* Exposed to Texas City Sediment at 30‰S

105. *P. pugio* also failed to accumulate Cd from Corpus Christi sediment at 15‰ and 30‰ (Figures 54 and 55). At all sampling times, tissue Cd levels were near the analytical detection limit and never above about 0.4 mg/kg. In animals exposed to sediment for 8 days and then returned to sediment-free seawater for 8 days, Cd levels were higher at the latter than at the former sampling time.

106. *Palaemonetes kadiakensis*. Cadmium concentrations in the tissues of *P. kadiakensis* exposed to Ashtabula sediment in fresh water rose steadily from 0.30 mg/kg on day 0 to 0.48 mg/kg on day 32 (Figure 56). The Cd concentrations in the control shrimp showed a similar rise from 0.03 mg/kg on day 0 to 0.25 mg/kg on day 20. Because of mortalities and other factors, there were sufficient animals available for only a single tissue sample at days 15 and 20 in the control group and at days 20 and 32 in the exposure group. No 32-day control sample was available. Perhaps in part because of this lack of replicates at the longer exposure times, statistical analysis revealed a lack of significance for exposure and time in the patterns of tissue Cd distribution observed.

107. *Neanthes arenaceodentata*. Accumulation of Cd by the worm *N. arenaceodentata* was not significantly affected by exposure to Texas City sediment at 30‰. There was a definite trend among both the control and exposed worms for tissue Cd concentrations to increase with time (as indicated by the significant effect of time) with the levels in the controls being higher than those in the sediment-exposed

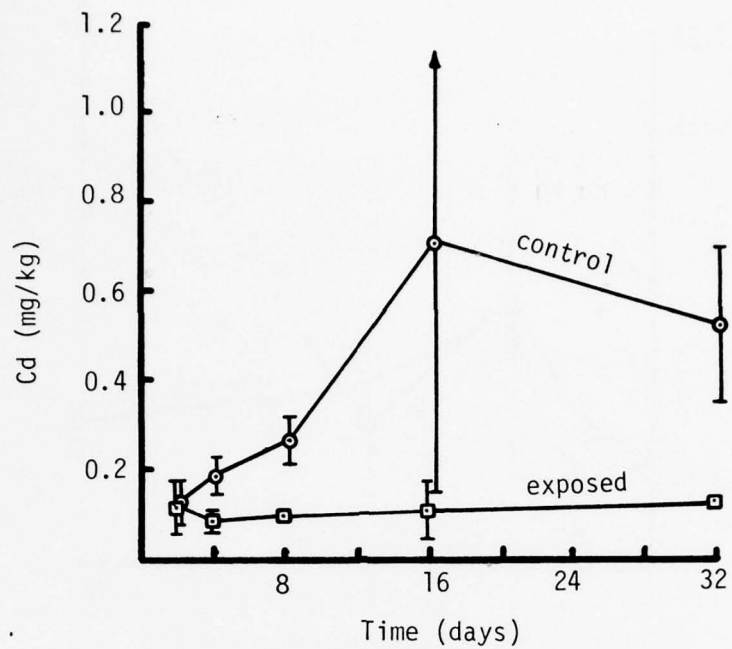


Figure 53. Mean Cd Uptake by *Palaemonetes pugio*
Exposed to Texas City Sediment at 15‰S

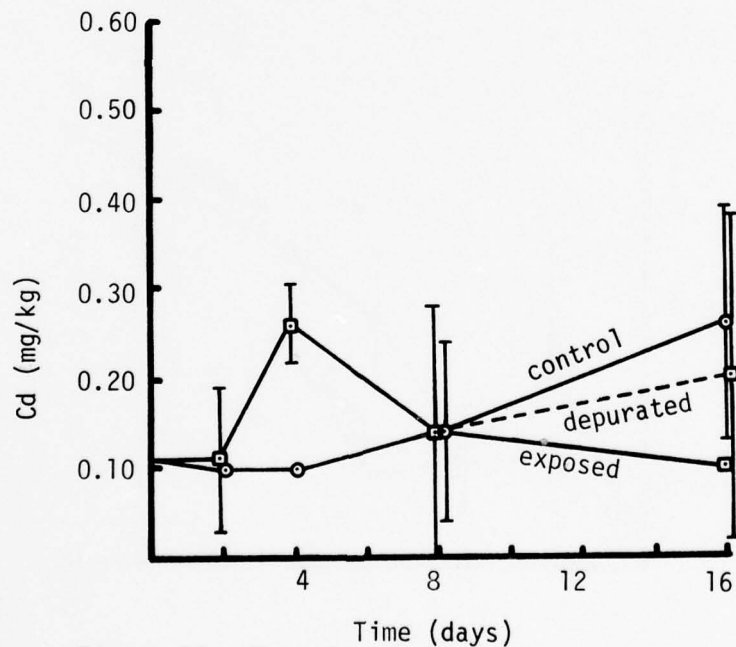


Figure 54. Mean Cd Uptake by *Palaemonetes pugio*
Exposed to Corpus Christi Sediment at 15‰S

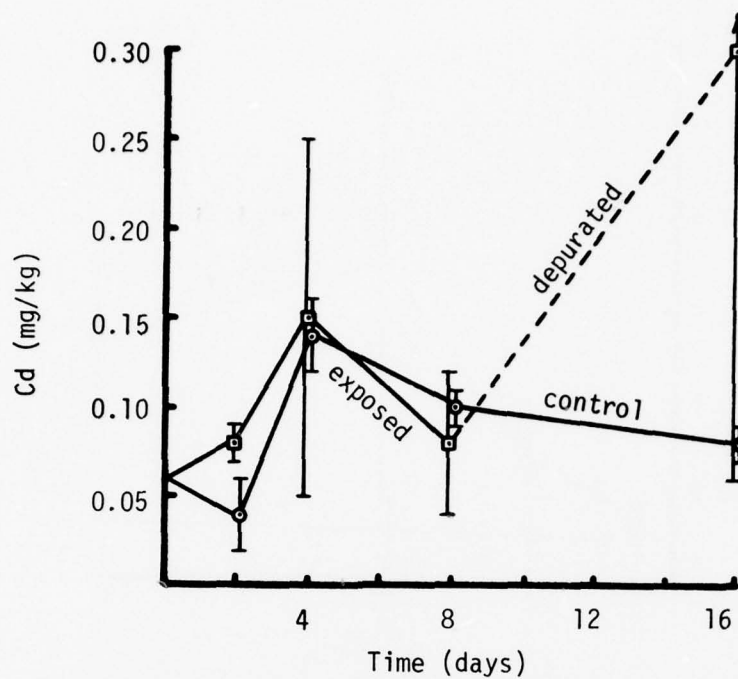


Figure 55. Mean Cd Uptake by *Palaemonetes pugio*
Exposed to Corpus Christi Sediment at 30‰S

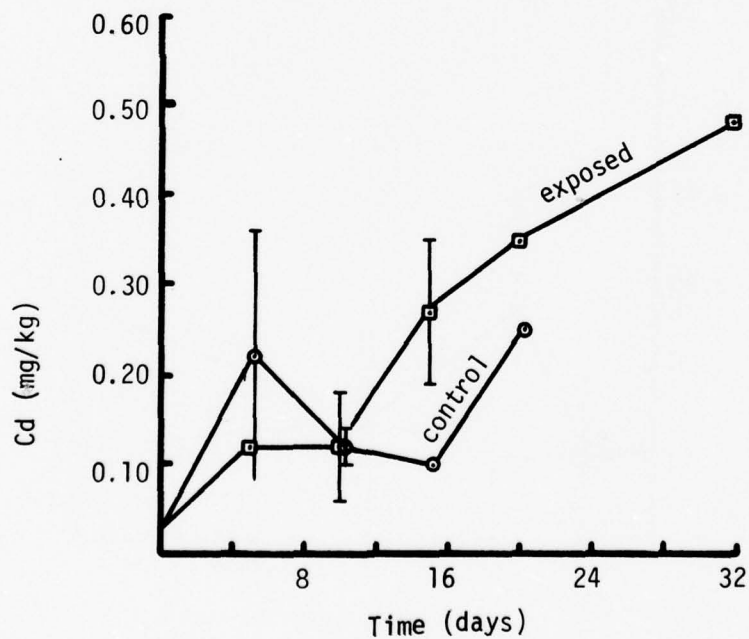


Figure 56. Mean Cd Uptake by *Palaemonetes kadia-*
kensis Exposed to Ashtabula Sediment in fresh water

animals at all sampling times except day 2 (Figure 57). Animals allowed to depurate for 8 days following 8 days exposure to the sediment had higher tissue Cd levels than the 8-day exposed animals.

108. Both exposure and time, but not their interaction, had a significant effect on the accumulation of Cd by *N. arenaceodentata* exposed to Corpus Christi sediment at 30‰S. In a second experiment, exposure was marginally insignificant ($P > F = 0.09$). In the first experiment, tissue Cd concentrations in sediment-exposed worms rose from 0.42 mg/kg to a mean of 7.7 mg/kg in 32 days, while Cd levels in the control worms rose only to 1.4 mg/kg in the same time period (Figure 58). In the second experiment, there was little change in Cd levels in control and sediment-exposed worms. However, at the last sampling time, day 16, the controls contained significantly higher Cd concentrations than did the exposed worms (Figure 59). There was a drop in tissue Cd concentrations from 0.15 mg/kg to 0.05 mg/kg during 8 days depuration following 8 days exposure to the sediment.

109. *Tubifex* sp. Both controls and worms exposed to Ashtabula sediment in fresh water showed erratic variations with time in tissue Cd concentrations (Figure 60). Mean tissue Cd concentrations varied from 0.02 mg/kg to 0.17 mg/kg. Time and exposure were without significant effect on the temporal patterns of tissue Cd concentrations. Animals allowed to depurate for 2 or 8 days following 8 days exposure to sediment showed a decrease in tissue Cd concentration.

Nickel (Ni)

110. Statistical analyses of Ni accumulation by all species are

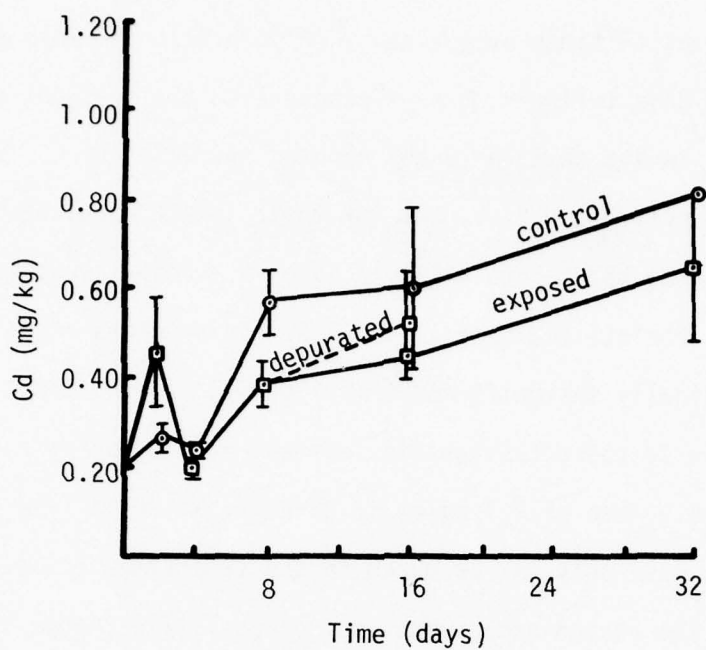


Figure 57. Mean Cd Uptake by *Neanthes arenaeodentata* Exposed to Texas City Sediment at 30‰S

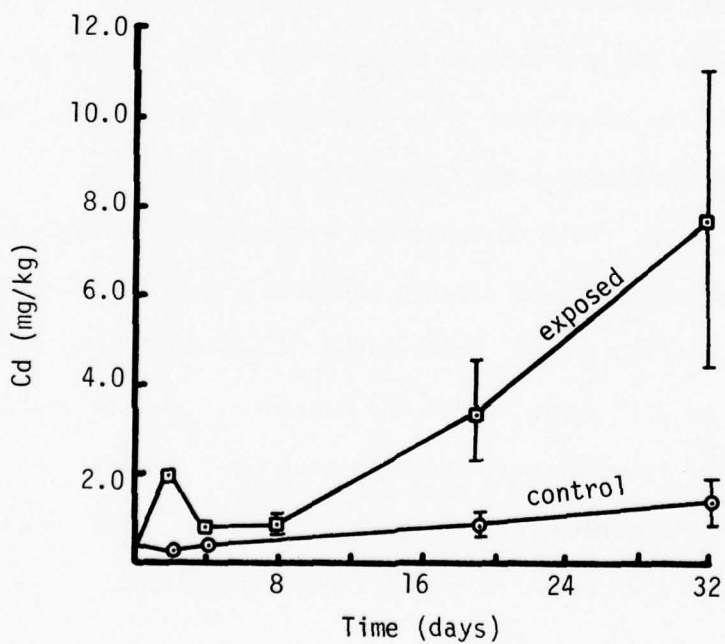


Figure 58. Mean Cd Uptake by *Neanthes arenaeodentata* Exposed to Corpus Christi Sediment at 30‰S [First Run]

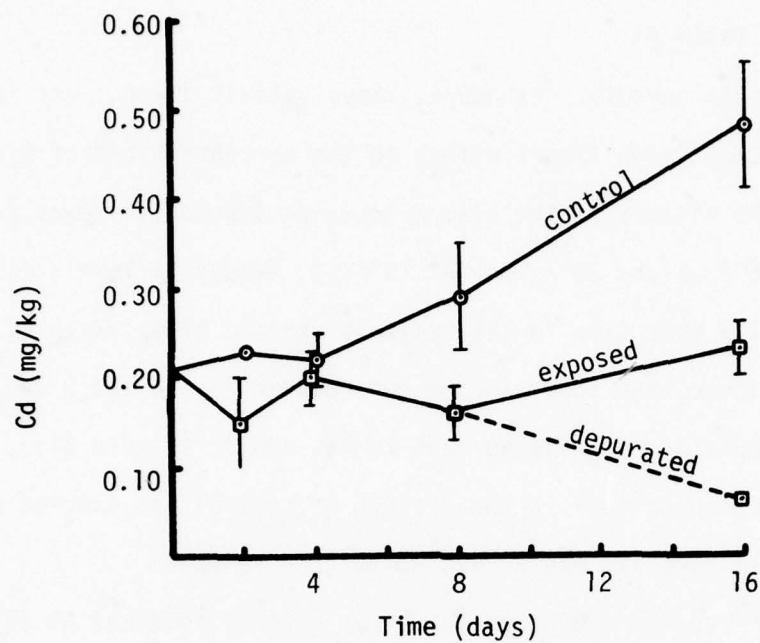


Figure 59. Mean Cd Uptake by *Neanthes arenaeodentata* Exposed to Corpus Christi Sediment at 30‰S [Second Run]

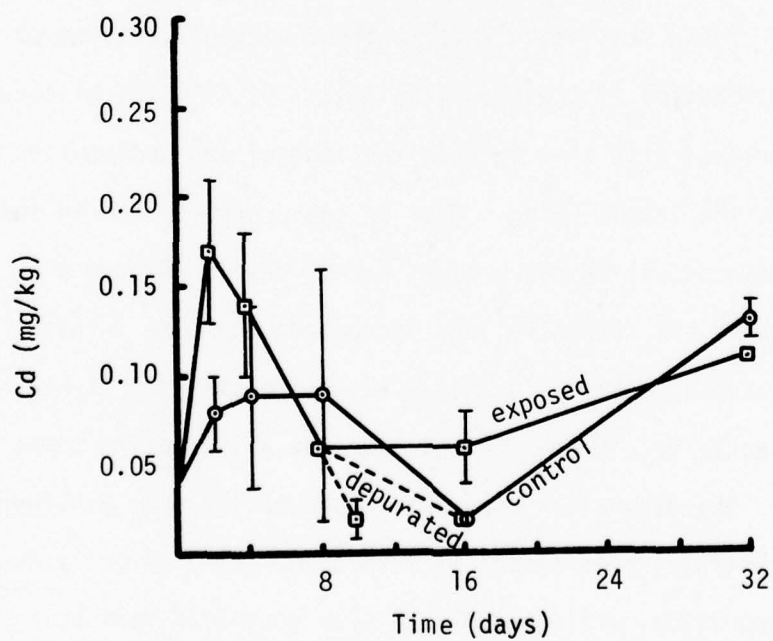


Figure 60. Mean Cd Uptake by *Tubifex* sp. Exposed to Ashtabula Sediment in fresh water

summarized in Table A5.

111. *Rangia cuneata*. Exposure, time, salinity, and their interactions were without significant effect on the concentrations of Ni measured in the tissues of the clam *R. cuneata* exposed to Texas City sediment at 15‰ and 30‰. At 15‰, tissue Ni levels fluctuated erratically over time in the sediment-exposed clams, with Ni levels being lower than those in the controls on days 4 and 8 and higher than those of controls on days 2, 16, and 32 (Figure 61). At 30‰, Ni concentrations in the tissues of control and exposed clams fluctuated in a parallel manner over time (Figure 62).

112. In *R. cuneata* exposed to Corpus Christi sediment at 15‰ and 30‰, exposure was without significant effect on Ni uptake. However, salinity, time, and the three first order interactions were significant. These statistics reflect the divergent patterns of temporal Ni distribution at the two salinities. At 15‰, Ni concentrations increased with time in both the control and sediment-exposed animals, with the levels being higher in the controls than in the exposed animals at all sampling times except day 16 (Figure 63). At 30‰, however, Ni concentrations decreased with time in both the control and exposed clams, with Ni levels being slightly higher, but not significantly so, in the control clams at all sampling times (Figure 64). The depuration experiments showed the same divergent trends. At 15‰, mean tissue Ni levels increased slightly during 8 days of depuration, while at 30‰ they decreased during the same depuration period.

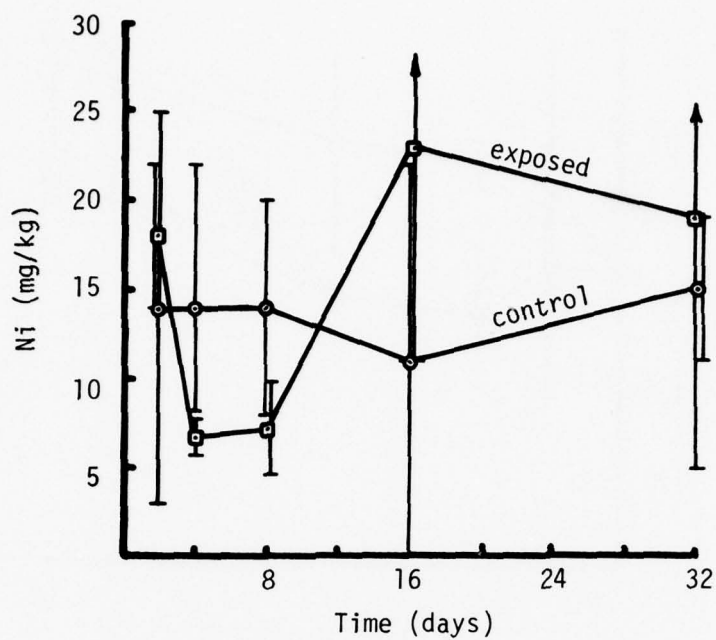


Figure 61. Mean Ni Uptake by *Rangia cuneata*
Exposed to Texas City Sediment at 15‰S

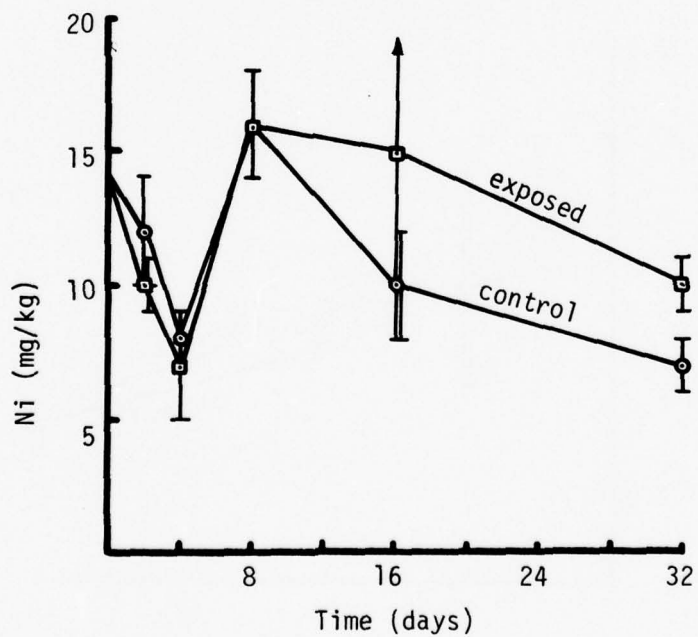


Figure 62. Mean Ni Uptake by *Rangia cuneata*
Exposed to Texas City Sediment at 30‰S

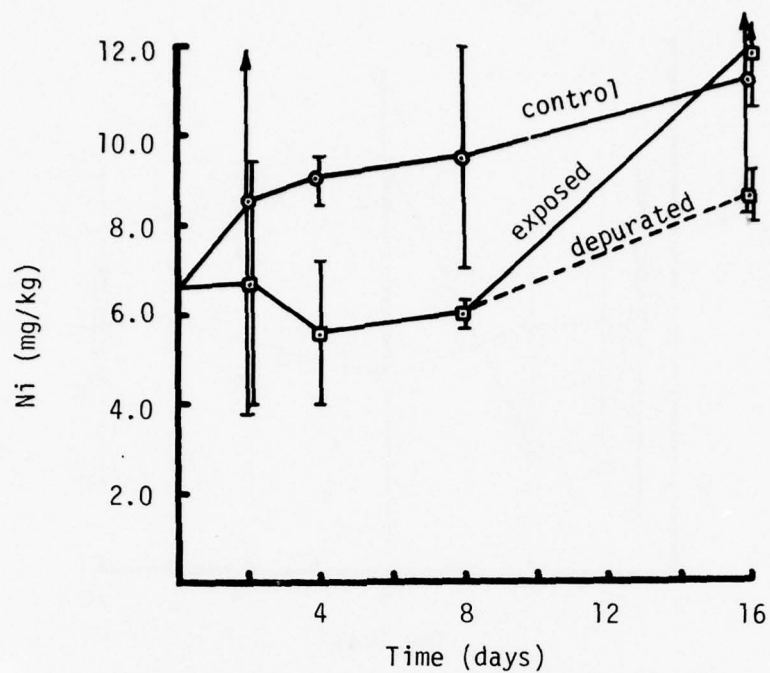


Figure 63. Mean Ni Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 15‰S

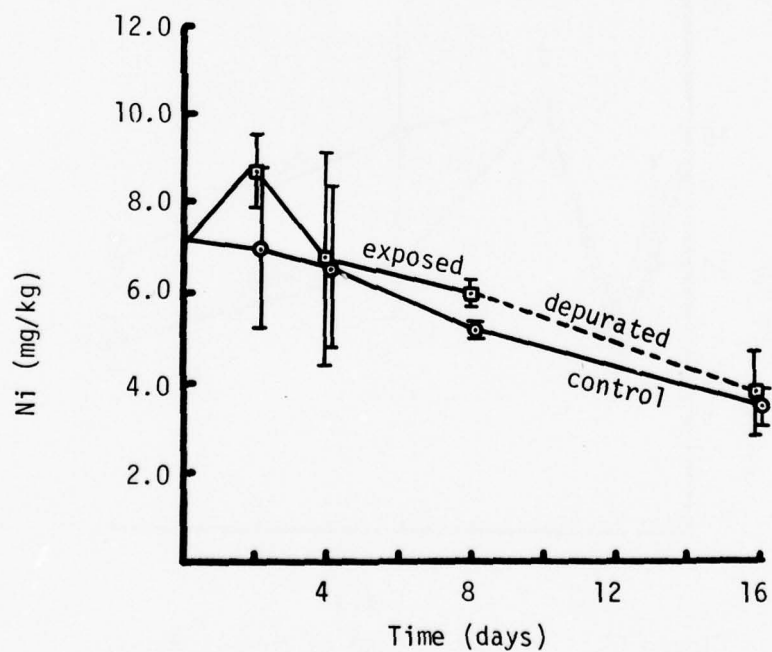


Figure 64. Mean Ni Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 30‰S

113. *R. cuneata* exposed to Ashtabula sediment in fresh water failed to show a significant effect of either exposure or time on tissue Ni concentrations. Nickel concentrations were similar in control and exposed animals at most sampling times, and there was a slight trend for Ni levels to decrease with time (Figure 65).

114. *Palaemonetes pugio*. With one exception (day 16 at 15‰), Ni concentrations in the tissues of shrimp *P. pugio* exposed to Texas City sediment at 15‰ and 30‰ were lower than those in the corresponding controls at all sampling times (Figures 66 and 67). In fact, at all sampling times in the 30‰ experiment and at the first three sampling times in the 15‰ experiment, Ni concentrations in the exposed animals were at or below the detection limit for the sample size available. Although statistical analysis revealed a significant effect of exposure on Ni accumulated, this was undoubtedly due to the higher Ni levels recorded in the control than in the exposed shrimp. Mean Ni concentrations were significantly higher in control and exposed shrimp at 30‰ than in those at 15‰.

115. The same phenomenon was observed in *P. pugio* exposed to Corpus Christi sediment at 15‰ and 30‰. At both salinities, Ni concentrations in the sediment-exposed animals were at or below the detection limit at all sampling times except the last one, day 16 (Figures 68 and 69). In both experiments, tissue Ni concentrations in the control shrimp rose to a peak at day 8 and then dropped sharply to lower values at day 16. Thus, although exposure had a significant effect on Ni uptake, inspection of the figures reveals that the cor-

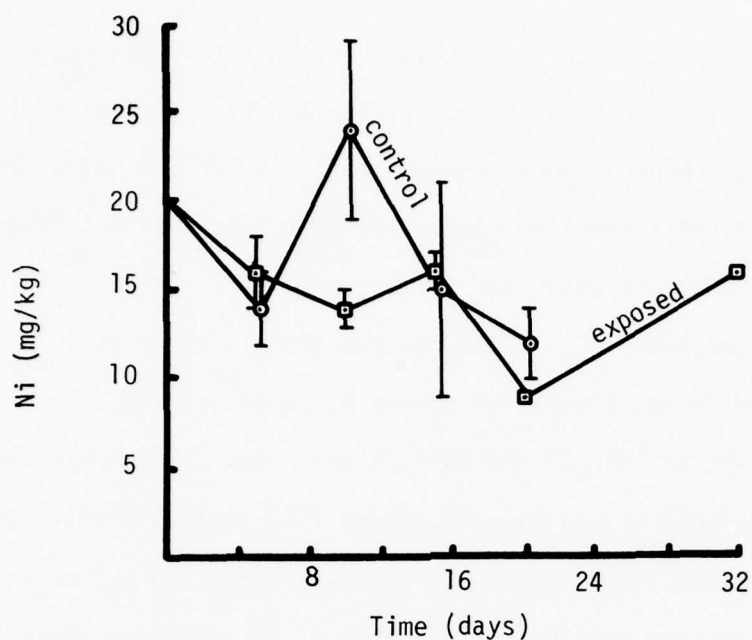


Figure 65. Mean Ni Uptake by *Rangia cuneata* Exposed to Ashtabula Sediment in fresh water

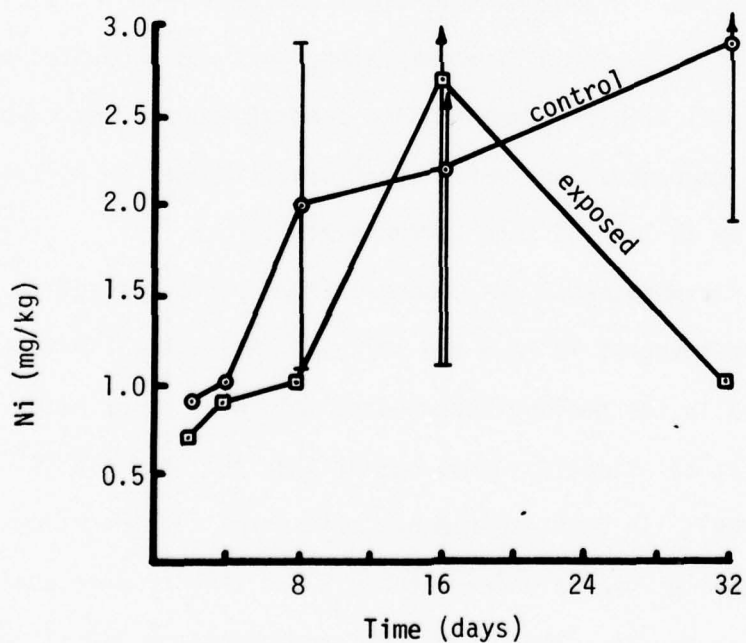


Figure 66. Mean Ni Uptake by *Palaemonetes pugio* Exposed to Texas City Sediment at 15‰S

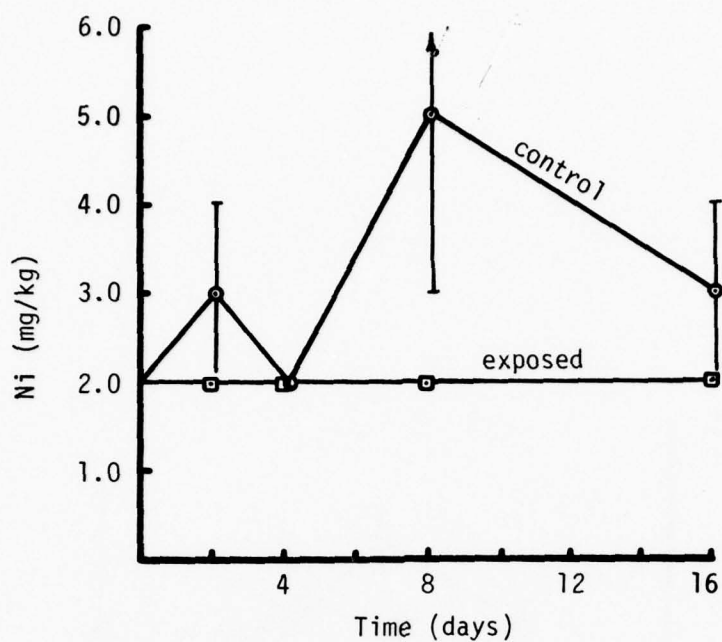


Figure 67. Mean Ni Uptake by *Palaemonetes pugio*
Exposed to Texas City Sediment at 30‰ S

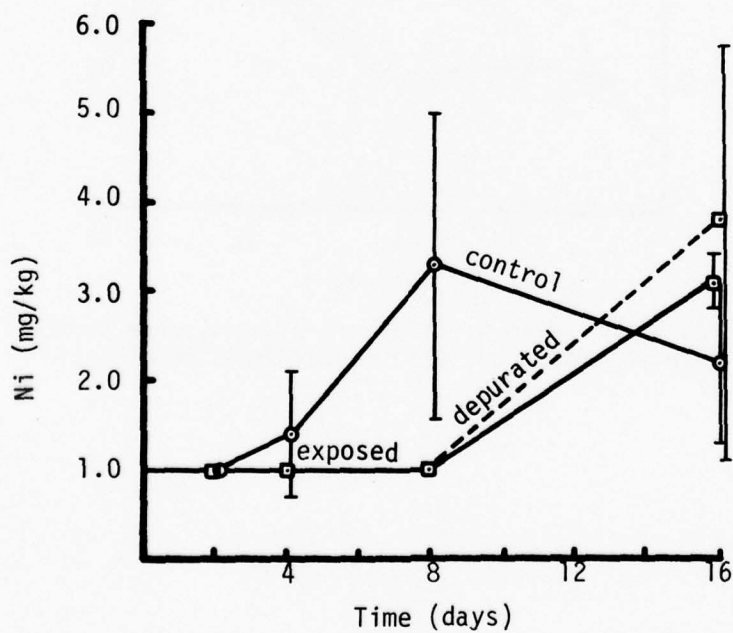


Figure 68. Mean Ni Uptake by *Palaemonetes pugio*
Exposed to Corpus Christi Sediment at 15‰ S

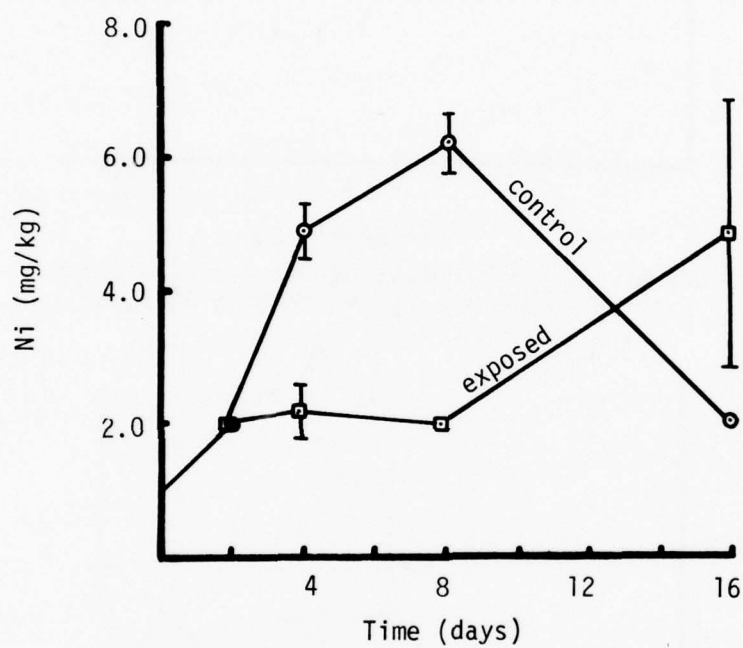


Figure 69. Mean Ni Uptake by *Palaemonetes pugio*
Exposed to Corpus Christi Sediment at 30‰S

relation was inverse. Salinity and the interaction of exposure and salinity were also statistically significant, reflecting the higher mean Ni concentrations in animals at 30‰S than at 15‰S.

116. *Palaemonetes kadiakensis*. This inverse relationship between sediment exposure and Ni uptake was seen again in *P. kadiakensis* exposed to Ashtabula sediment in fresh water (Figure 70). Control shrimp had significantly higher tissue Ni levels than exposed shrimp at all sampling times except day 32. On day 32, no control sample was available for analysis and only one exposed shrimp sample was available. This single sample had a higher Ni concentration than any previous sample.

117. *Neanthes arenaceodentata*. Accumulation of Ni by the worm *N. arenaceodentata* was not significantly affected by time or exposure to Texas City sediment at 30‰S. However, Ni concentrations in exposed worms showed a definite rising trend from 3.8 mg/kg on day 2 to 10 mg/kg on day 32, while tissue Ni levels in the controls showed a slight decrease from 5.8 mg/kg to 4.0 mg/kg in the same time period (Figure 71). A longer exposure time might have resulted in significant Ni accumulation. There was practically no change in tissue Ni concentrations during 8 days depuration following 8 days exposure to the sediment.

118. Roughly similar trends in tissue Ni concentration changes were observed in the two experiments in which *N. arenaceodentata* were exposed to Corpus Christi sediment at 30‰S (Figures 72 and 73). In both cases, Ni concentrations in control and exposed worms tended to

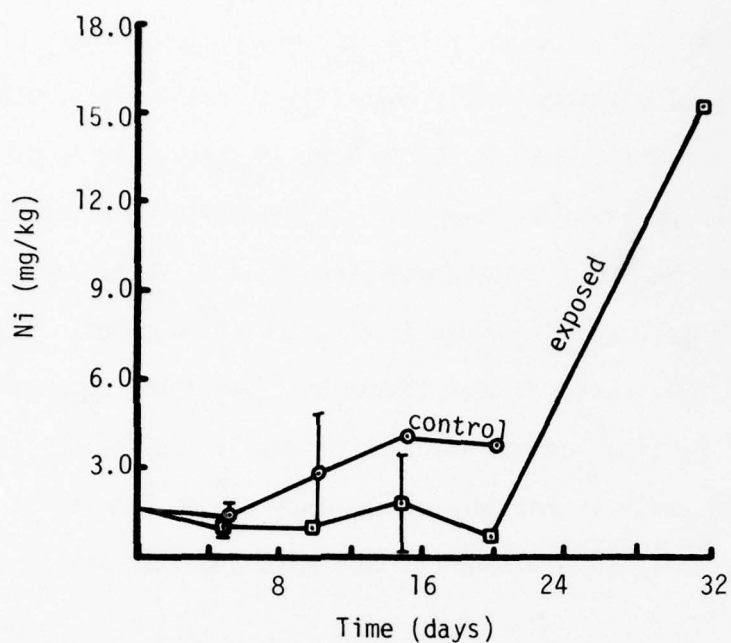


Figure 70. Mean Ni Uptake by *Palaemonetes kadiakensis* Exposed to Ashtabula Sediment in fresh water

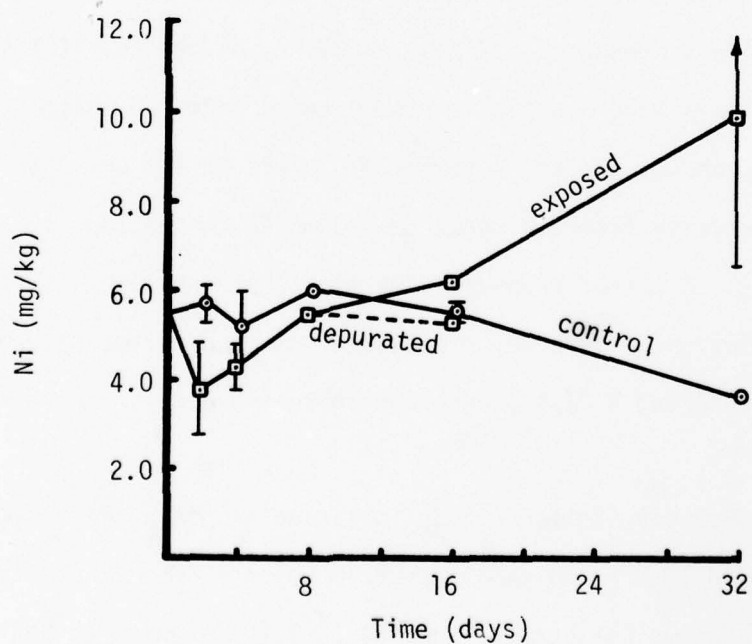


Figure 71. Mean Ni Uptake by *Neanthes arenaeodentata* Exposed to Texas City Sediment at 30‰S

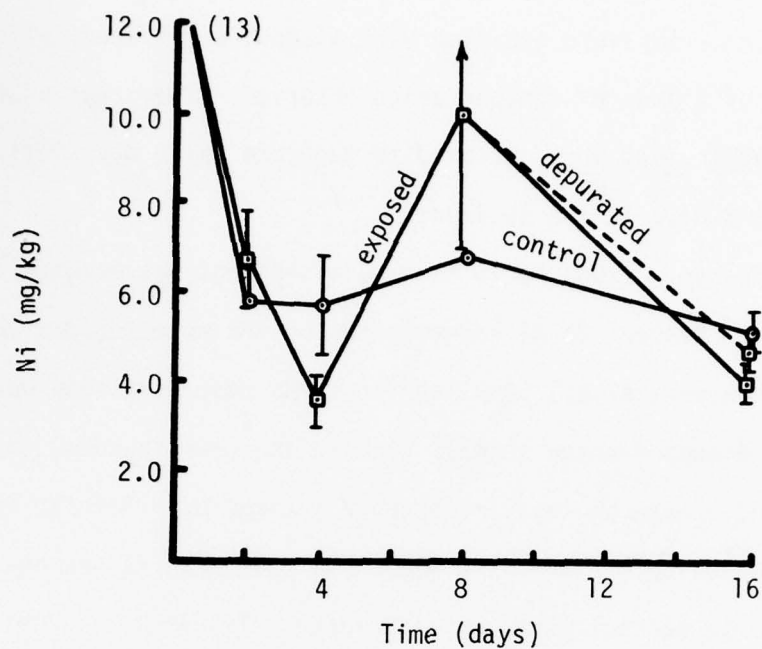


Figure 72. Mean Ni Uptake by *Neanthes arenaeodentata* Exposed to Corpus Christi Sediment at 30‰S [First Run]

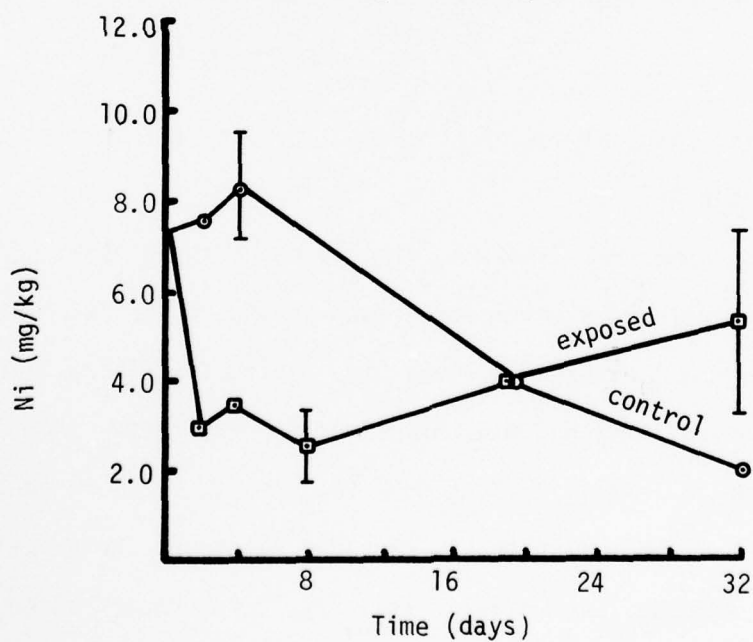


Figure 73. Mean Ni Uptake by *Neanthes arenaeodentata* Exposed to Corpus Christi Sediment at 30‰S [Second Run]

decrease with time. Exposure and time were without significant effect on the patterns of tissue Ni concentration observed. There was a drop in tissue Ni levels among worms allowed to depurate for 8 days following exposure for 8 days to the sediment.

119. *Tubifex* sp. Exposure to Ashtabula sediment was marginally insignificant with respect to Ni accumulation by the worm *Tubifex* sp. ($P > F = 0.07$). However, at all sampling times, Ni concentrations were higher in the sediment-exposed animals than in the corresponding controls (Figure 74). Mean Ni levels reached a maximum of 2.3 mg/kg in the exposed worms on days 2 and 4, while the maximum mean Ni concentration measured in control worms was 1.5 mg/kg. Tissue Ni concentrations dropped from 1.0 mg/kg to less than 1 mg/kg during 2 to 8 days depuration following 8 days exposure to the sediment.

Lead (Pb)

120. Statistical analyses of Pb accumulation by all species are summarized in Table A6.

121. *Rangia cuneata*. Exposure, time, and the three first-order interactions were without significant effect on the accumulation of Pb by the clam *R. cuneata* exposed to Texas City sediment at 15‰ and 30‰. However salinity had a highly significant effect on the tissue concentrations of Pb. At 15‰, tissue Pb concentrations in control and exposed clams were similar at all sampling times and varied between 0.3 mg/kg and 1.2 mg/kg (Figure 75). At 30‰, Pb concentrations were temporally more variable and mean concentrations ranged from 0.9 mg/kg to 2.3 mg/kg (Figure 76).

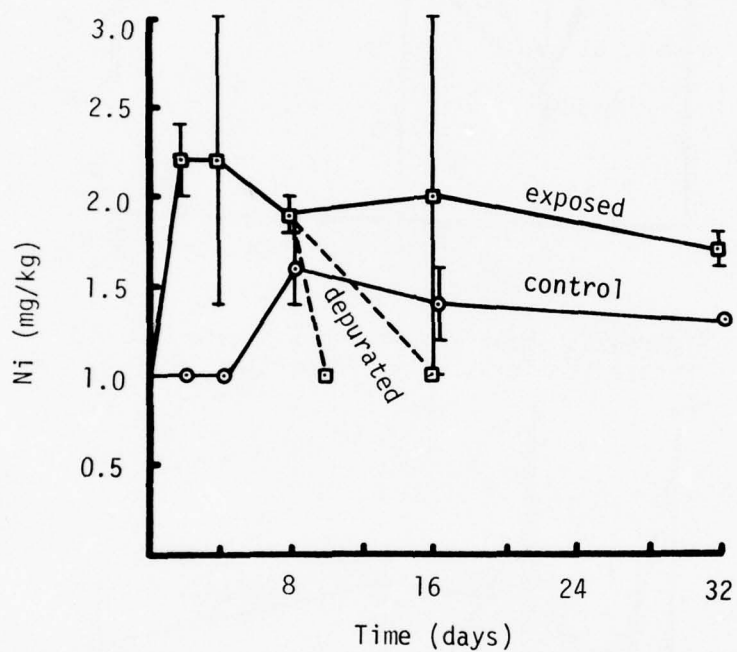


Figure 74. Mean Ni Uptake by *Tubifex* sp.
Exposed to Ashtabula Sediment

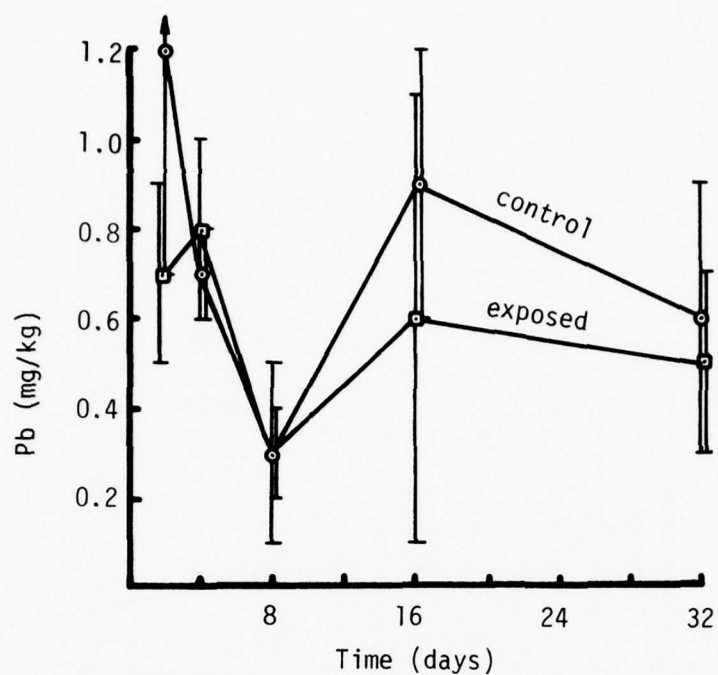


Figure 75. Mean Pb Uptake by *Rangia cuneata*
Exposed to Texas City Sediment at 15‰S

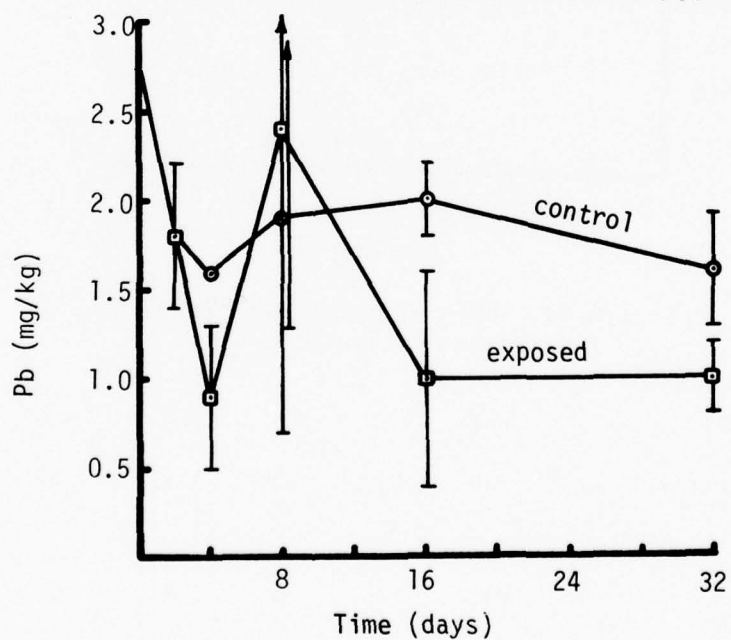


Figure 76. Mean Pb Uptake by *Rangia cuneata*
Exposed to Texas City Sediment at 30‰S

122. A similar pattern of Pb distribution was observed in *R. cuneata* exposed to Corpus Christi sediment at 15‰ and 30‰. Exposure, time, and the three first-order interactions did not contribute significantly to the Pb levels observed, but the main effect of salinity was significant. Again, Pb concentrations in the control and exposed clams at 15‰ were lower than those in clams at 30‰ (Figures 77 and 78). At 15‰, tissue Pb concentrations in the control clams were at or below the detection limit of 0.1 mg/kg at all sampling times, while Pb levels in sediment-exposed clams rose from less than 0.1 mg/kg to 0.27 mg/kg during 16 days of exposure. At 30‰, tissue Pb concentrations in the control exposed clams fluctuated in a cyclic and parallel fashion during the time course of the experiment. Lead levels in exposed clams were always higher than those in the corresponding controls and reached a peak of 2.4 mg/kg on day 8. Animals allowed to depurate for 8 days following 8 days exposure to the sediment showed a small drop in mean tissue Pb burdens at 15‰ and a large drop at 30‰.

123. There was little difference in tissue Pb concentrations between control and exposed *R. cuneata* during the first 15 days of exposure to Ashtabula sediment in fresh water. However, on day 20, the mean Pb concentration in the exposed clams was significantly higher (3.0 mg/kg) than that in the controls (0.8 mg/kg) (Figure 79). Exposure alone did not contribute significantly to the results. However, time and the interaction of exposure and time were significant.

124. *Palaemonetes pugio*. The shrimp *P. pugio* failed to accumulate

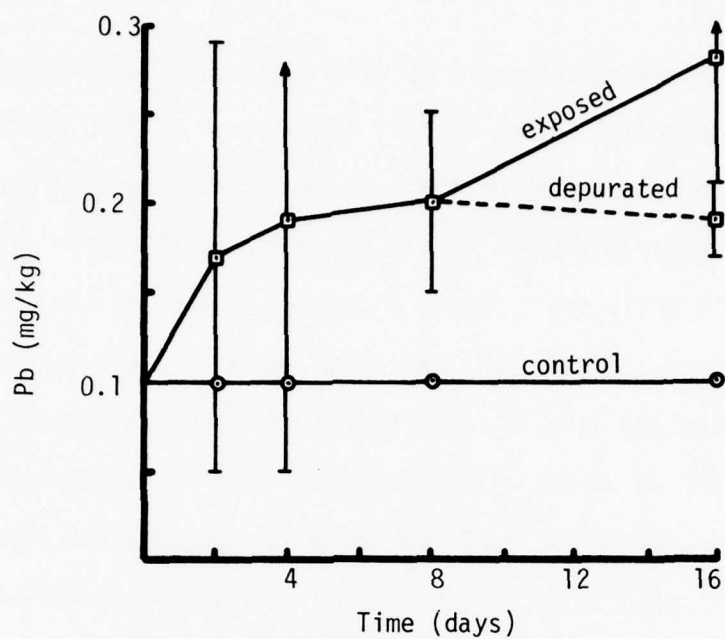


Figure 77. Mean Pb Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 15‰S

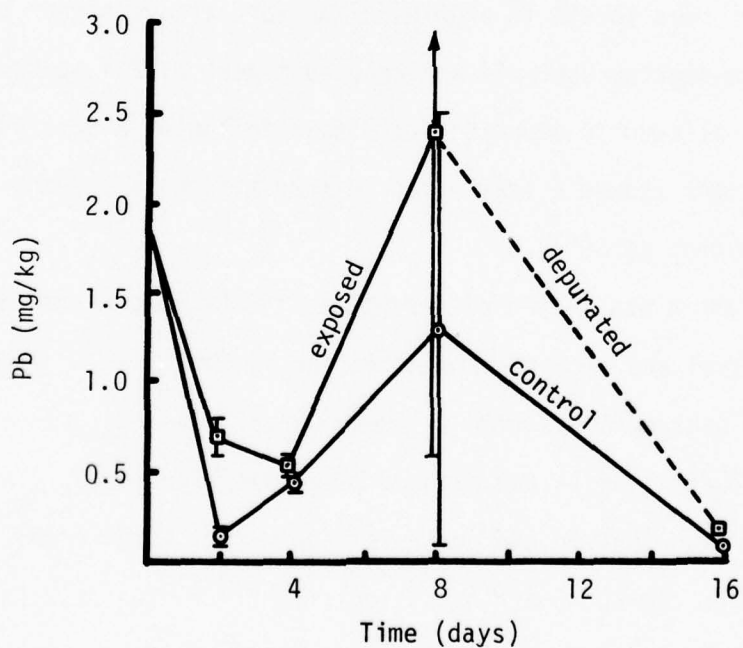


Figure 78. Mean Pb Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 30‰S

Pb from Texas City sediment at either 15‰ or 30‰. None of the main effects or their interactions were statistically significant. At 15‰, tissue Pb concentrations in the exposed shrimp dropped steadily from 0.5 mg/kg on day 2 to 0.1 mg/kg on day 32, while Pb levels in the control shrimp fluctuated cyclically between 0.3 mg/kg and 0.6 mg/kg (Figure 80). At 30‰, sediment-exposed shrimp had tissue Pb levels at or below the detection limit of 0.5 mg/kg at all sampling times, while Pb levels in the controls remained at or below 1 mg/kg at all sampling times except day 4, when a mean level of 5.2 mg/kg was measured (Figure 81).

125. Quite different results were obtained in *Palaemonetes pugio* exposed to Corpus Christi sediment at 15‰ and 30‰. Exposure, salinity, and their interaction significantly affected Pb uptake, while time and its interaction with the other main effects were not significant. At 15‰, mean Pb concentrations in exposed shrimp rose from less than 0.1 mg/kg on day 4 to 0.34 mg/kg on day 16, while concentrations in the control animals remained less than 0.1 mg/kg at all sampling times (Figure 83). At 30‰, mean tissue Pb concentrations in control shrimp remained in the 0.2 mg/kg to 0.5 mg/kg range throughout the experimental period, while those in the exposed shrimp rose from 0.3 mg/kg on day 0 to 3.4 mg/kg on day 8, the last day for which an exposed shrimp sample was available (Figure 83). At 15‰, shrimp which were allowed to depurate for 8 days following 8 days exposure showed an increase in tissue Pb levels, while at 30‰, the 8-day depurated shrimp showed a moderate decrease in tissue Pb levels.

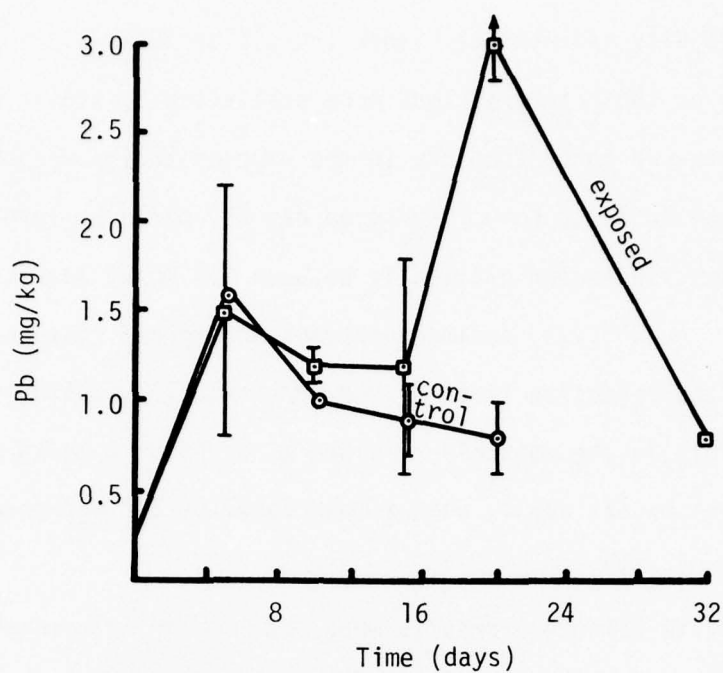


Figure 79. Mean Pb Uptake by *Rangia cuneata*
Exposed to Ashtabula Sediment in fresh water

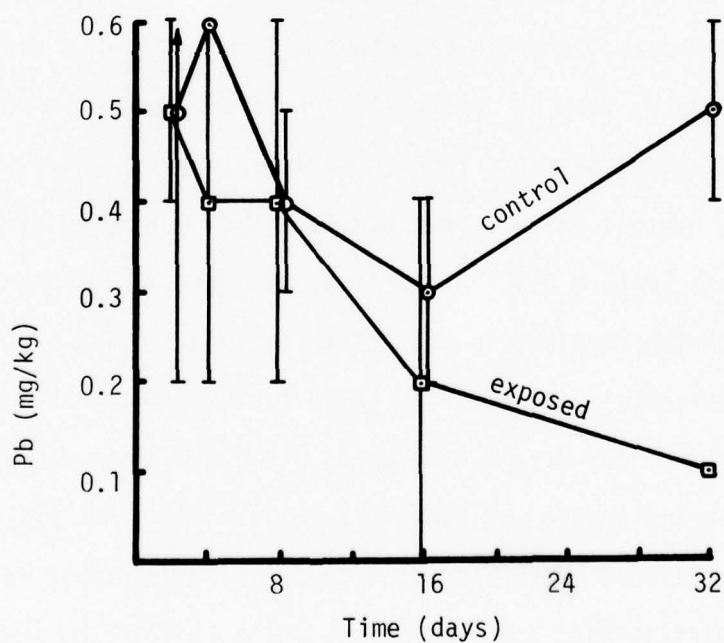


Figure 80. Mean Pb Uptake by *Palaemonetes pugio*
Exposed to Texas City Sediment at 15‰S

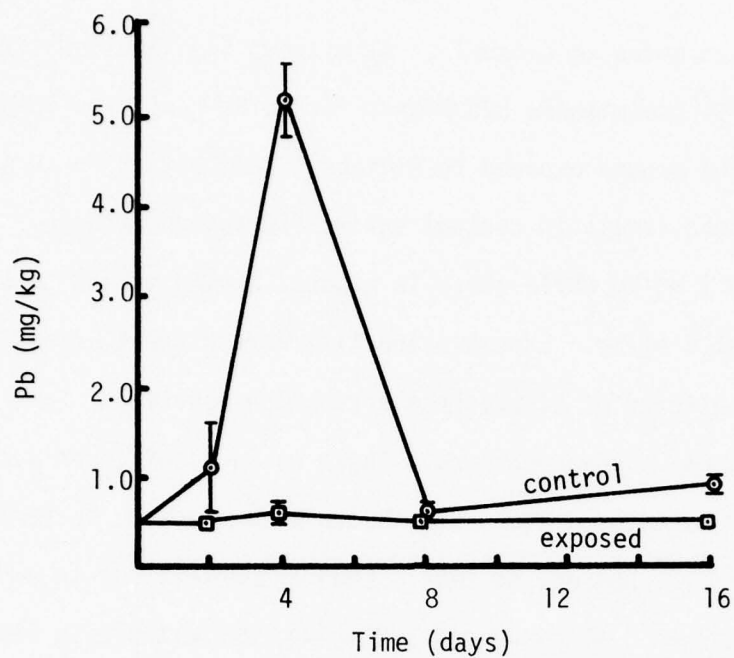


Figure 81. Mean Pb Uptake by *Palaemonetes pugio*
Exposed to Texas City Sediment at 30‰S

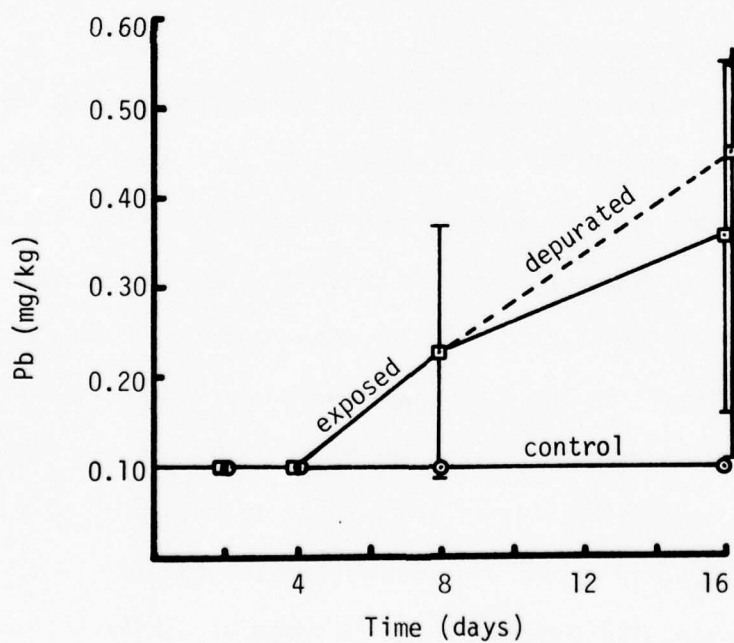


Figure 82. Mean Pb Uptake by *Palaemonetes pugio*
Exposed to Corpus Christi Sediment at 15‰S

126. *Palaemonetes kadiakensis*. At all but one sampling time, control shrimp *P. kadiakensis* had higher tissue Pb concentrations than the corresponding groups exposed to Ashtabula sediment in fresh water (Figure 84). Lead levels in control shrimp fluctuated between 0.42 mg/kg to 4.1 mg/kg while those in exposed shrimp varied between 0.42 mg/kg and 1.6 mg/kg. Exposure and time were without significant effect on the patterns of tissue Pb distribution observed.

127. *Neanthes arenaceodentata*. There was a significant accumulation of Pb by *N. arenaceodentata* attributable to exposure to Texas City sediment at 30‰, but not to time. Lead concentrations in control worms varied between 0.65 mg/kg and 1.2 mg/kg, while those in exposed animals increased from 1 mg/kg on day 0 to 2 mg/kg on day 32 (Figure 84). Eight days of depuration resulted in a drop in mean tissue Pb concentrations from 1.2 mg/kg to 0.8 mg/kg.

128. In the two experiments in which *N. arenaceodentata* were exposed to Corpus Christi sediment at 30‰, there was a highly significant accumulation of Pb attributable to exposure, time, and their interaction. In both experiments, Pb concentrations in the controls remained relatively constant during the time course of the experiment, with the day 0 levels in the first experiment approximately twice those in the second experiment (Figures 86 and 87). In the first experiment, tissue Pb concentrations in the exposed animals reached a maximum of 16 mg/kg on days 2 and 19. In the second experiment, tissue Pb levels rose steadily to a maximum of 8 mg/kg at day 16. Tissue Pb levels dropped from 4 mg/kg to 1 mg/kg during 8 days depuration follow-

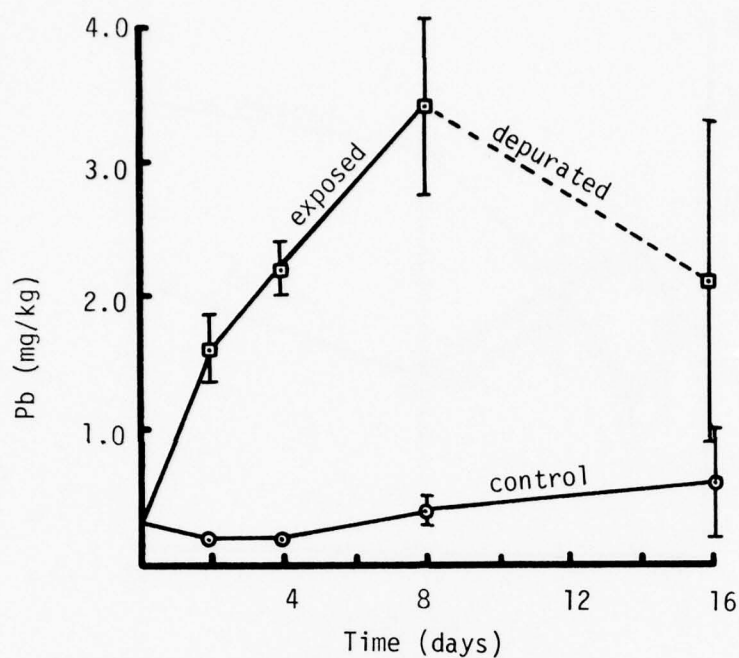


Figure 83. Mean Pb Uptake by *Palaemonetes pugio*
Exposed to Corpus Christi Sediment at 30‰S

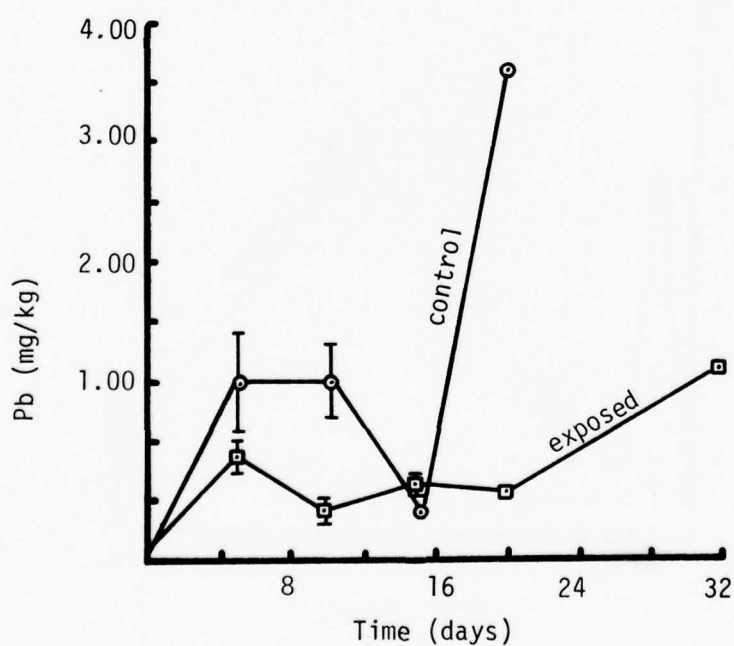


Figure 84. Mean Pb Uptake by *Palaemonetes kadiakensis*
Exposed to Ashtabula Sediment in fresh water

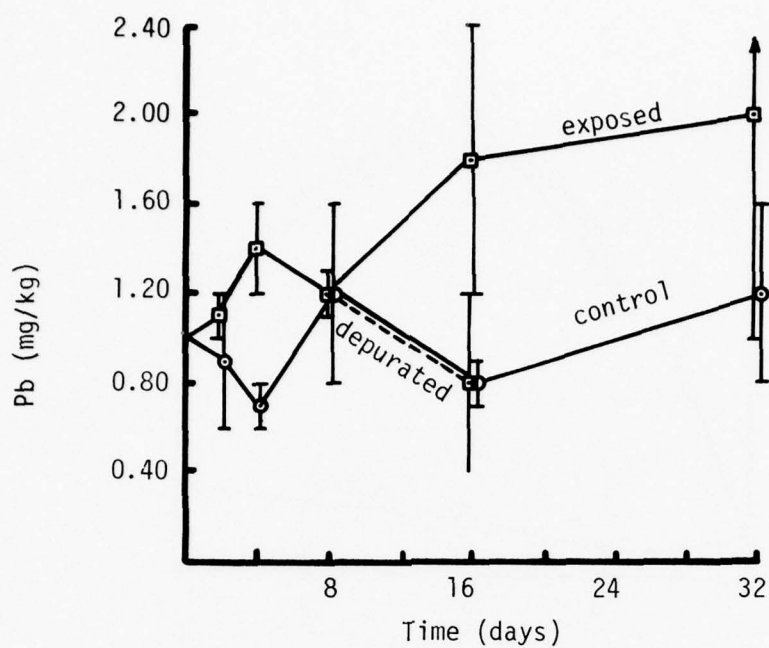


Figure 85. Mean Pb Uptake by *Neanthes arenaceodentata* Exposed to Texas City Sediment at 30‰ S

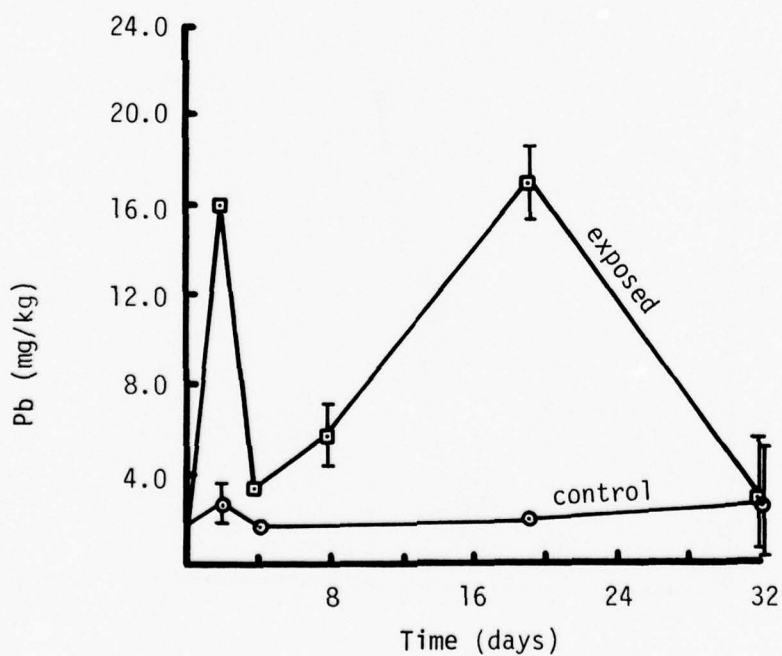


Figure 86. Mean Pb Uptake by *Neanthes arenaceodentata* Exposed to Corpus Christi Sediment at 30‰ S [First Run]

ing 8 days exposure to the sediment.

129. *Tubifex* sp. exposed to Ashtabula sediment in fresh water contained significantly higher concentrations of Pb than the corresponding controls at all sampling times. Time was without significant effect on the Pb concentrations measured. Mean tissue Pb concentrations in exposed animals varied from 4.0 mg/kg to 5.6 mg/kg, while those in controls varied from 2.2 mg/kg to 4.3 mg/kg, suggesting that the differences observed were due to a decrease in Pb levels in the controls and not to a net uptake of Pb by the exposed worms (Figure 88). Lead levels in 8-day-exposed worms increased slightly during 2 to 8 days depuration in sediment-free fresh water.

Zinc (Zn)

130. Statistical analyses of Zn accumulation by all species are summarized in Table A7.

131. *Rangia cuneata*. Exposure, time, their interactions with each other, and their interactions with salinity were without significant effect on Zn uptake by the clam *R. cuneata* during exposure to Texas City sediment at 15‰ and 30‰. However, salinity had a significant effect on Zn concentrations in the clam tissues. At each salinity, there was little difference in tissue Zn concentrations between exposed animals and the corresponding controls (Figures 89 and 90). At 15‰, mean Zn concentrations in the clam tissues ranged from 75 mg/kg to 97 mg/kg, while at 30‰, mean tissue Zn levels ranged from 60 mg/kg to 83 mg/kg.

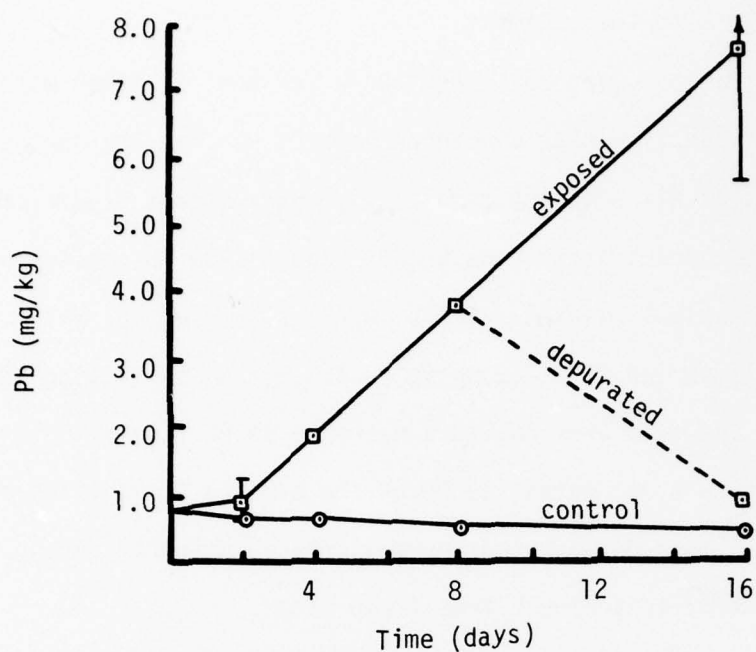


Figure 87. Mean Pb Uptake by *Neanthes arenaceodentata*
Exposed to Corpus Christi Sediment at 30‰S
[Second Run]

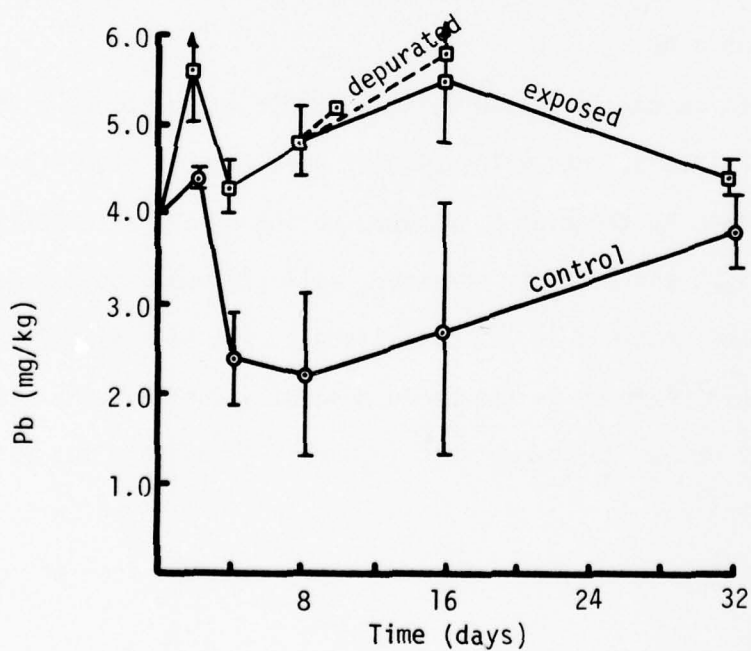


Figure 88. Mean Pb Uptake by *Tubifex sp.*
Exposed to Ashtabula Sediment in fresh water

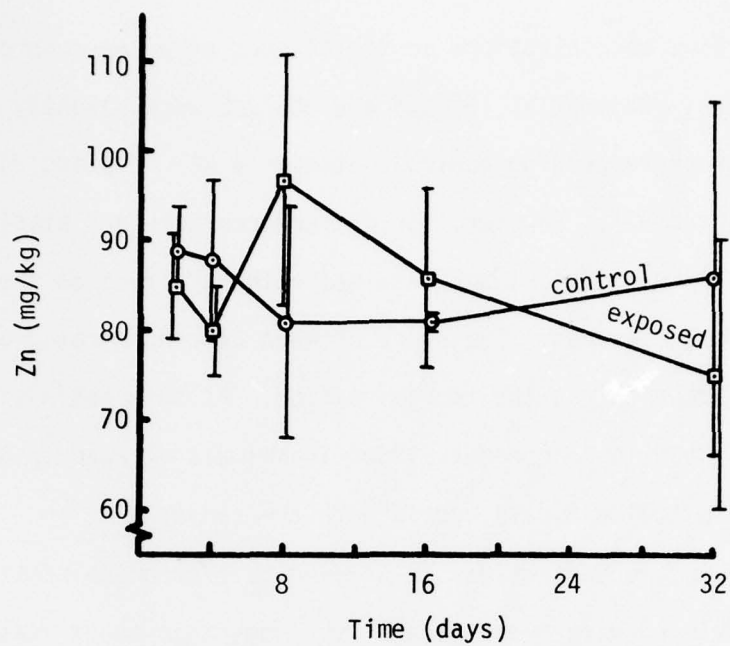


Figure 89. Mean Zn Uptake by *Rangia cuneata* Exposed to Texas City Sediment at 15‰S

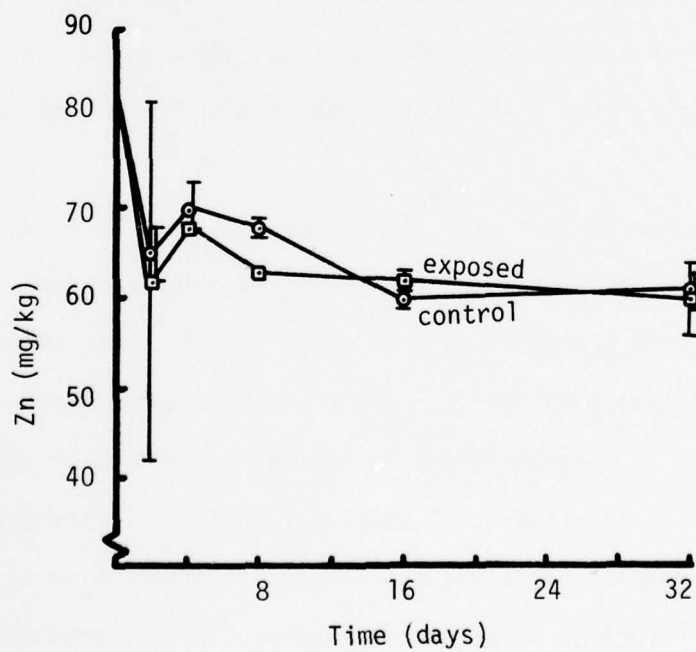


Figure 90. Mean Zn Uptake by *Rangia cuneata* Exposed to Texas City Sediment at 30‰S

132. Zinc concentrations in the tissues of *R. cuneata* exposed to Corpus Christi sediment at 15‰ and 30‰ were slightly higher than those in the corresponding controls at nearly all sampling times (Figures 91 and 92). However, the differences were not statistically significant. In addition, salinity was without effect on the tissue Zn concentrations measured. The range of mean Zn concentrations observed was almost identical at the two salinities. At both salinities, there was a small drop in Zn concentrations in animals allowed to depurate for 8 days following 8 days exposure to the sediment.

133. Zinc concentrations in *R. cuneata* exposed to Ashtabula sediment in fresh water were generally higher than those measured in clams exposed to Corpus Christi and Texas City sediments at higher salinities. However, Zn concentrations in control and exposed animals fluctuated in the same range, and there was not a significant effect of exposure, time, or their interaction on the concentrations measured (Figure 93).

134. *Palaemonetes pugio*. The concentrations of Zn in the tissues of the control shrimp *P. pugio* were equal to or higher than those in the corresponding groups exposed to Texas City sediment at both 15‰ and 30‰ (Figures 94 and 95). At both salinities there was a definite trend for Zn concentrations to increase with time in both the control and exposed animals. Statistical analysis of the results indicated that exposure, salinity, and their interaction were significant. However, the effect of exposure was inverse, as indicated above. Zinc concentrations in animals at 30‰ were slightly higher (range of

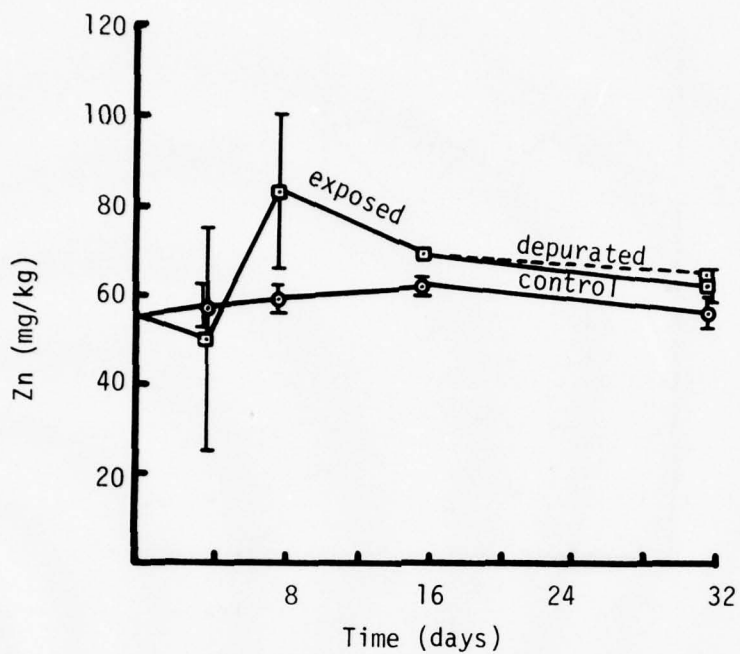


Figure 91. Mean Zn Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 15‰S

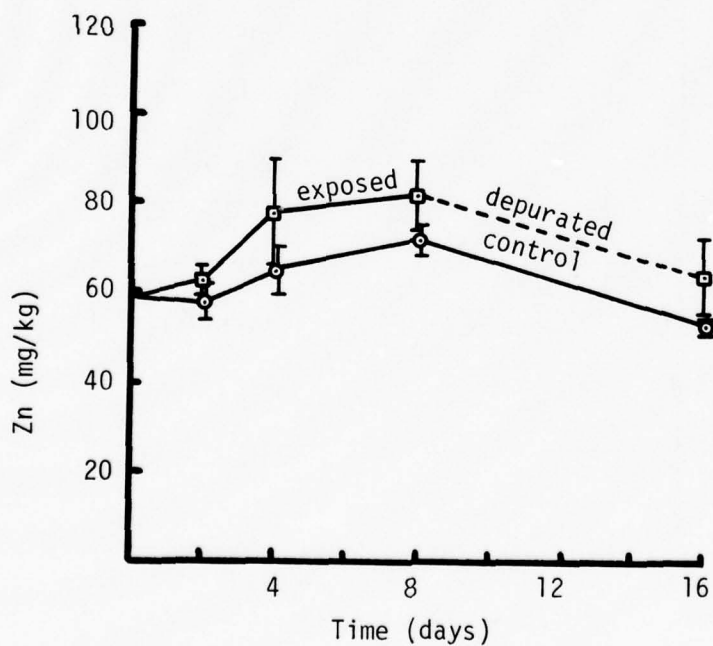


Figure 92. Mean Zn Uptake by *Rangia cuneata* Exposed to Corpus Christi Sediment at 30‰S

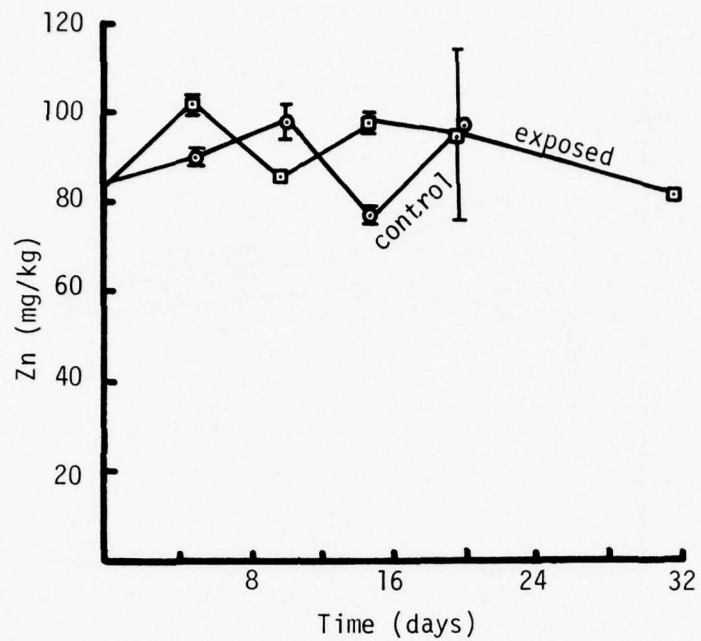


Figure 93. Mean Zn Uptake by *Rangia cuneata*
Exposed to Ashtabula Sediment in fresh water

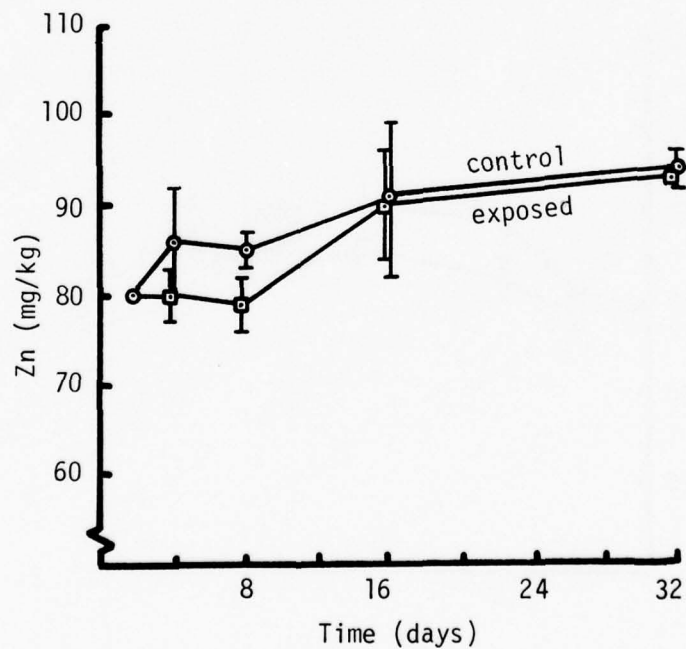


Figure 94. Mean Zn Uptake by *Palaemonetes pugio*
Exposed to Texas City Sediment at 15‰S

means, 73 mg/kg to 108 mg/kg) than those in animals at 15‰S (range of means, 79 mg/kg to 94 mg/kg).

135. Quite different results were obtained for *P. pugio* exposed to Corpus Christi sediment at 15‰S and 30‰S. In this case, sediment-exposed shrimp had higher mean Zn concentrations than the corresponding controls at all sampling times (Figures 96 and 97). There was no clear trend toward increasing or decreasing tissue Zn concentrations with time at either salinity. However, mean Zn concentrations in sediment-exposed shrimp at 15‰S were generally slightly higher than those in exposed shrimp at 30‰S. The main effects of exposure and time and the interaction of salinity and time were found to contribute significantly to the values recorded. At 15‰S, there was a small increase in Zn concentrations in shrimp during 8 days depuration following 8 days exposure to the sediment, while at 30‰S, there was a small decrease in Zn concentrations during a similar period.

136. *Palaemonetes kadiakensis*. The mean concentrations of Zn in the tissues of shrimp *P. kadiakensis* exposed to Ashtabula sediment in fresh water were lower than those in the corresponding controls at all sampling times (Figure 98). There was a definite trend toward increasing Zn concentrations with time in both the control and exposed animals. The main effects of exposure and time were both found to be significant. However, as can be seen from Figure 98, the effect of exposure was inverse.

137. *Neanthes arenaceodentata* and *Tubifex* sp. The worms

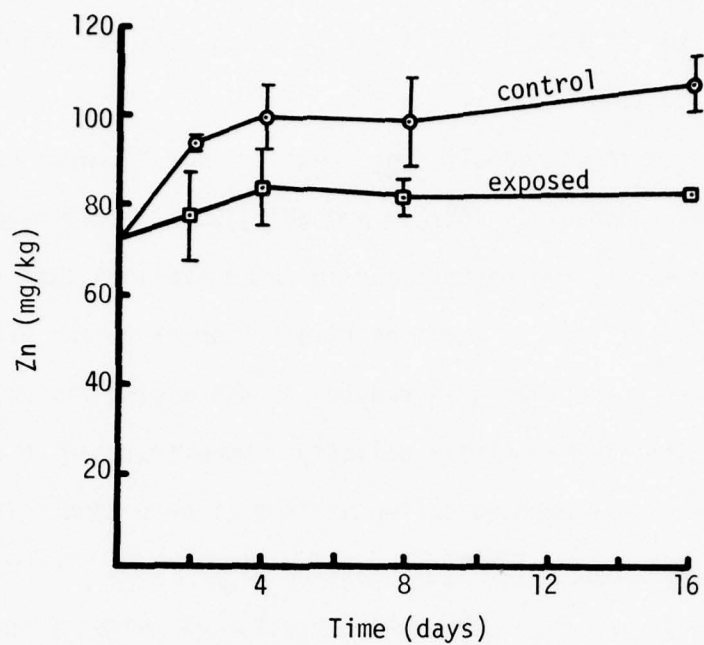


Figure 95. Mean Zn Uptake by *Palaemonetes pugio*
Exposed to Texas City Sediment at 30‰ S

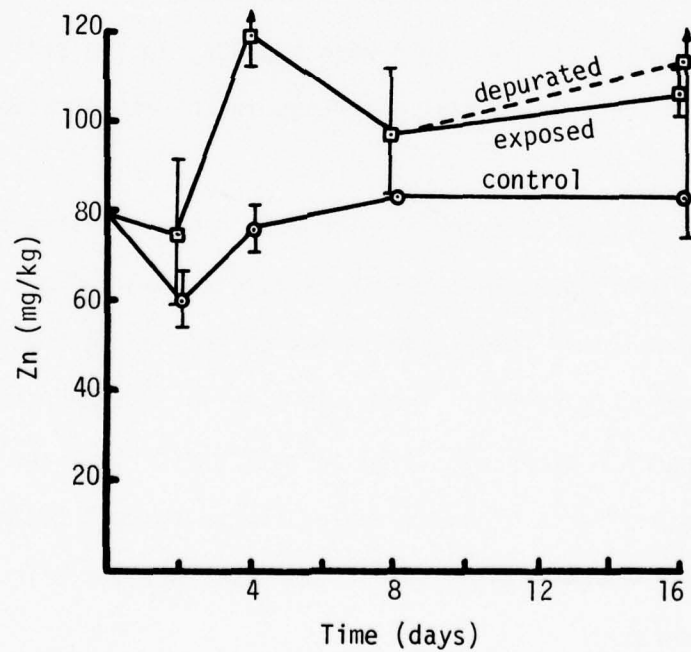


Figure 96. Mean Zn Uptake by *Palaemonetes pugio*
Exposed to Corpus Christi Sediment at 15‰ S

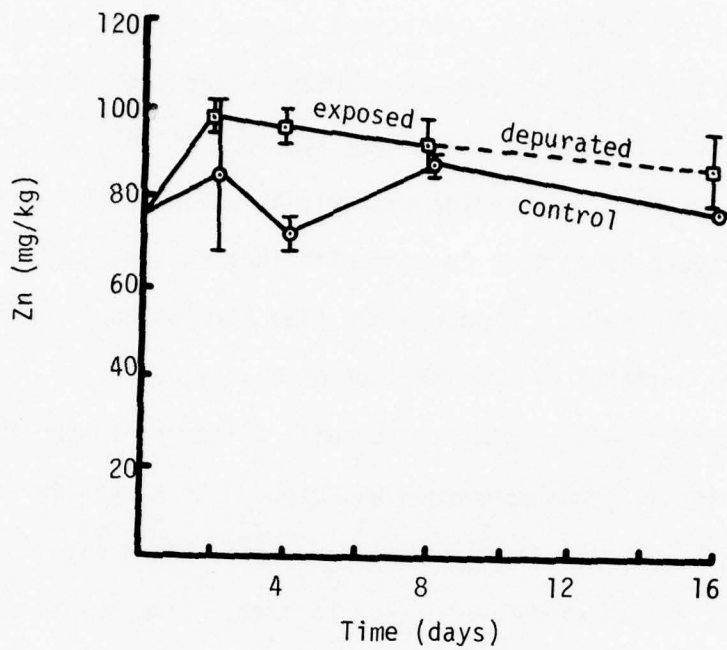


Figure 97. Mean Zn Uptake by *Palaemonetes pugio*
Exposed to Corpus Christi Sediment at 30‰S

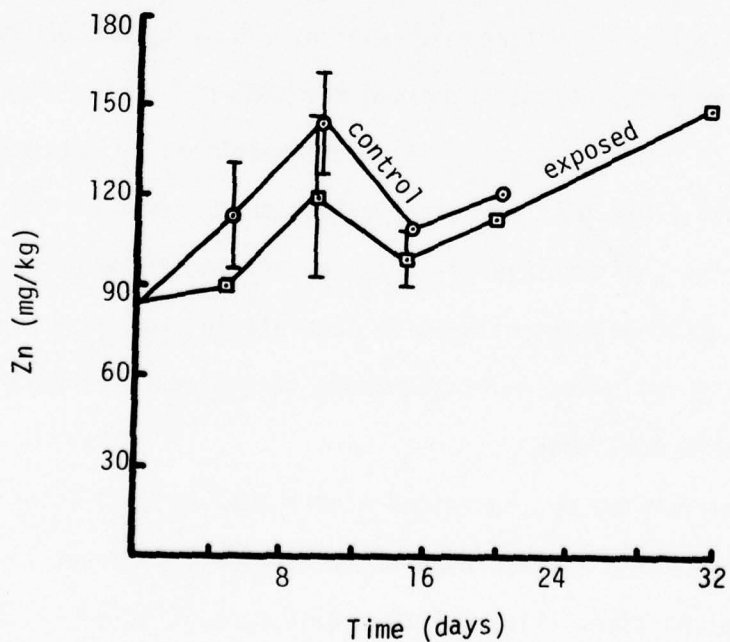


Figure 98. Mean Zn Uptake by *Palaemonetes kadia-*
kensis Exposed to Ashtabula Sediment in fresh water

N. arenaceodentata and *Tubifex* sp. contained substantially higher concentrations of Zn than did the clams and shrimp. Zinc concentrations in *N. arenaceodentata* exposed to Texas City sediment at 30‰S were similar to those in the corresponding controls and showed little variation with time (Figure 99). Mean Zn concentrations in these animals ranged from 167 to 247 mg/kg. Exposure and time were without significant effect on the patterns of Zn distribution observed.

138. The patterns of Zn uptake were quite different in the two experiments in which *N. arenaceodentata* was exposed to Corpus Christi sediment at 30‰S. In the first experiment, there was a significant accumulation of Zn due to exposure but not to time. Zinc levels in control animals remained relatively constant in the 182 mg/kg to 198 mg/kg range (Figure 100). However Zn concentrations in the exposed worms fluctuated cyclically between extremes of 276 mg/kg and 625 mg/kg. In the second experiment, neither exposure nor time had a significant effect on tissue Zn concentrations. Zinc concentrations in control and exposed animals fluctuated erratically between extremes of 110 mg/kg and 326 mg/kg during the time course of the experiment (Figure 101). Zinc concentrations in animals allowed to depurate in sediment-free seawater for 8 days following 8 days exposure to sediment showed an increase in Zn concentrations.

139. Control *Tubifex* sp. contained higher mean concentrations of Zn than the corresponding animals exposed to Ashtabula sediment in fresh water at all sampling times (Figure 102). Zinc concentrations in both the control and exposed animals increased gradually in an almost parallel

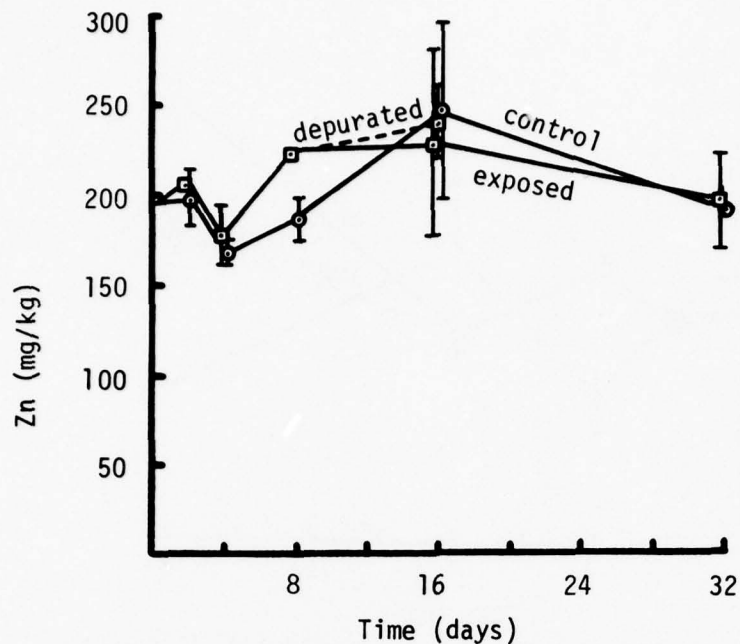


Figure 99. Mean Zn Uptake by *Neanthes arenaceodentata*
Exposed to Texas City Sediment at 30‰ S

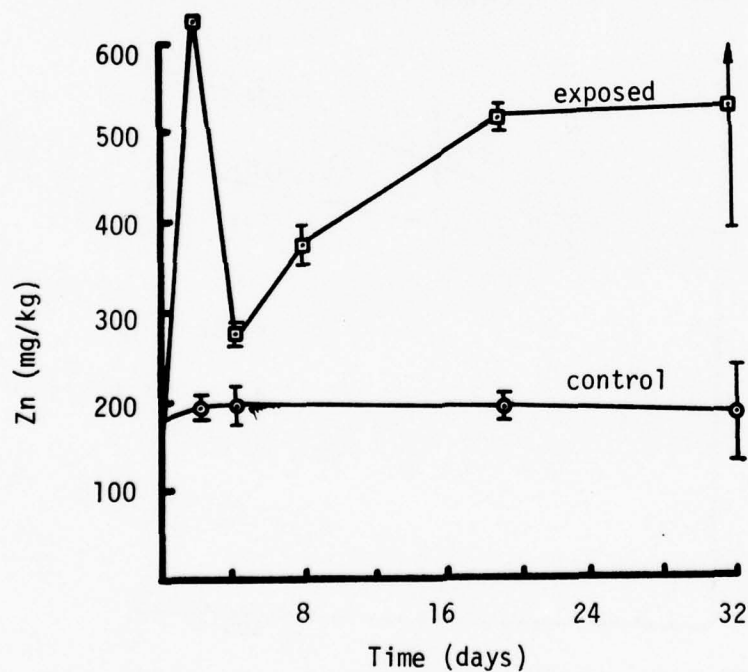


Figure 100. Mean Zn Uptake by *Neanthes arenaceodentata*
Exposed to Corpus Christi Sediment at 30‰ S
[First Run]

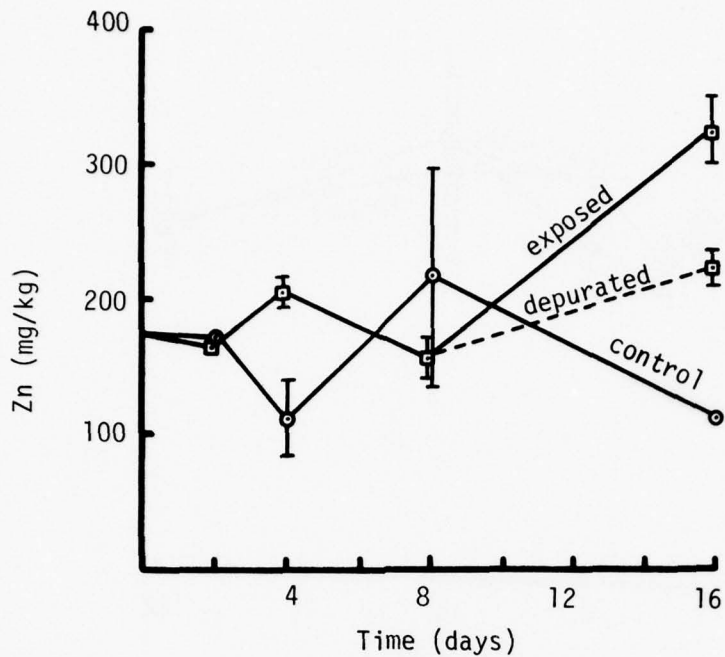


Figure 101. Mean Zn Uptake by *Neanthes arenaceodentata* Exposed to Corpus Christi Sediment at 30‰S [Second Run]

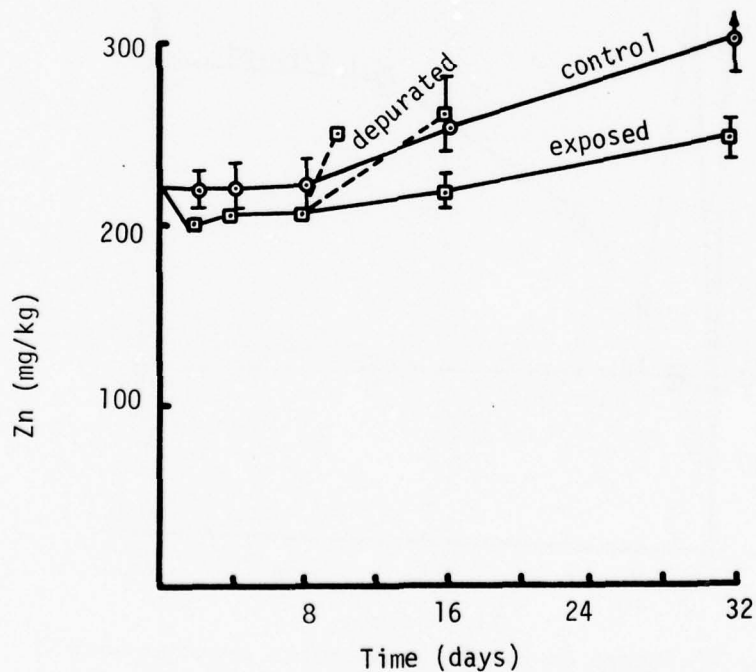


Figure 102. Mean Zn Uptake by *Tubifex* sp. Exposed to Ashtabula Sediment in fresh water

fashion during the timecourse of the experiment. Both exposure and time were found to contribute significantly to the results obtained. However, once again, the effect of exposure was inverse. Zinc concentrations increased in worms during 2 days and 8 days depuration following 8 days exposure to the sediment.

Chromium (Cr)

140. Statistical analyses of Cr accumulation by all species are summarized in Table A8.

141. *Rangia cuneata*. Salinity, but not exposure, time, or the three first-order interactions, had a significant effect on the concentrations of Cr in the tissues of clams *R. cuneata* exposed to Texas City sediment at 15‰ and 30‰. Chromium levels in control and exposed animals at 15‰ varied from 5.2 mg/kg to 6.9 mg/kg, while those in animals at 30‰ varied from 2.8 mg/kg to 5.2 mg/kg (Figures 103 and 104). There was no clear-cut temporal pattern of concentration at either salinity.

142. *R. cuneata* failed to accumulate Cr from Corpus Christi sediment at 15‰ and 30‰. None of the main effects or their interactions were significantly related to Cr levels measured. At both salinities, all mean Cr concentrations fell in the relatively narrow range of 2.7 mg/kg to 4.6 mg/kg (Figure 105 and 106).

143. *R. cuneata* exposed to Ashtabula sediment in fresh water failed to show a significant accumulation of chromium. However, as can be seen in Figure 107, exposed animals showed a nearly steady increase in tissue Cr concentrations from 4.1 mg/kg on day 0 to 11 mg/kg on day 20.

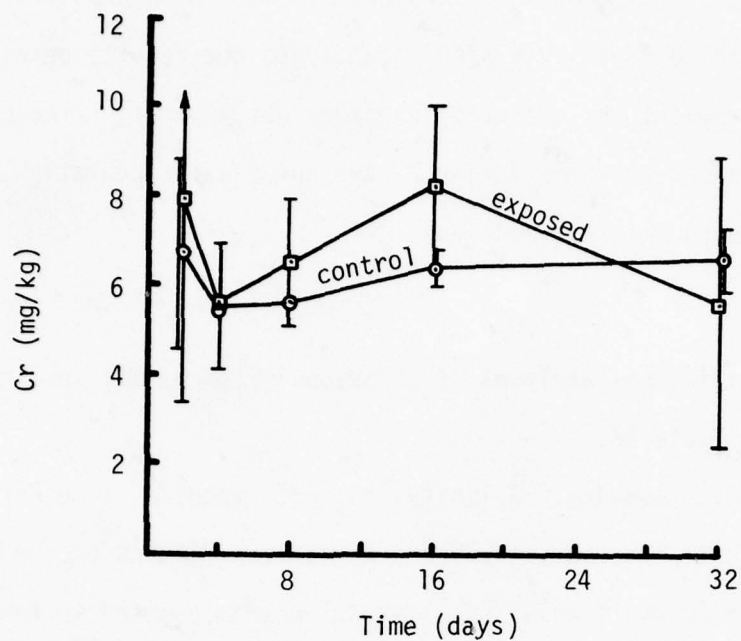


Figure 103. Mean Cr Uptake by *Rangia cuneata*
Exposed to Texas City Sediment at 15‰S

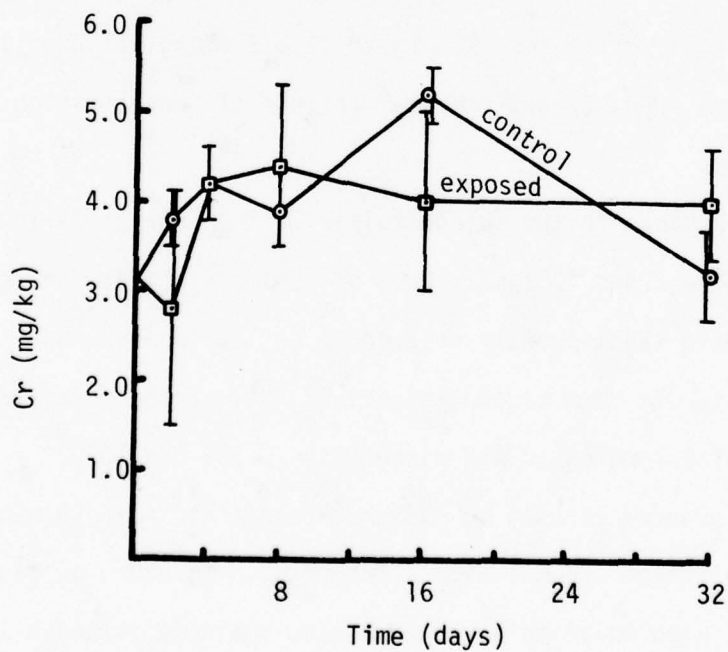


Figure 104. Mean Cr Uptake by *Rangia cuneata*
Exposed to Texas City Sediment at 30‰S

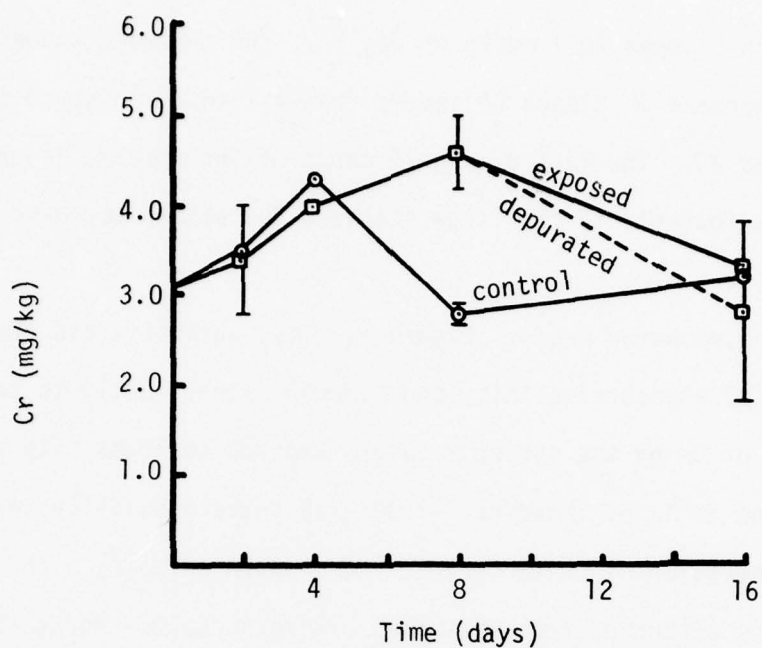


Figure 105. Mean Cr Uptake by *Rangia cuneata*
Exposed to Corpus Christi Sediment at 15‰S

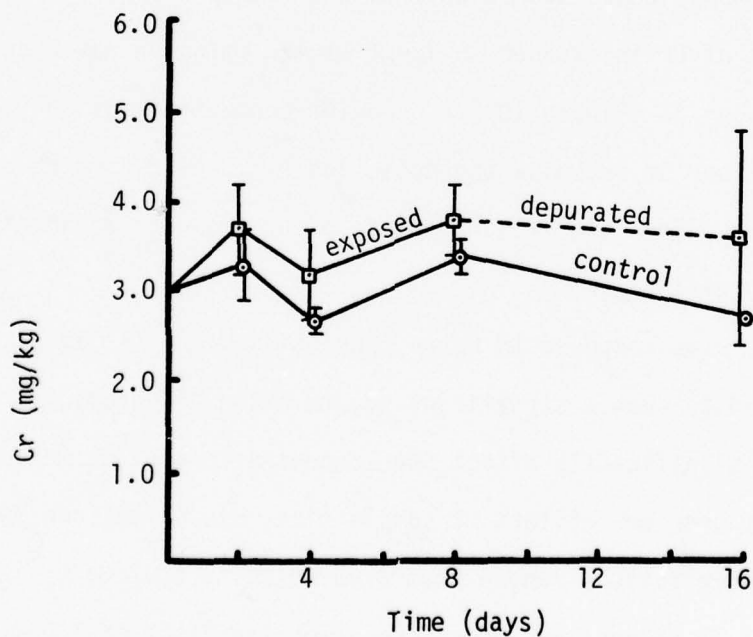


Figure 106. Mean Cr Uptake by *Rangia cuneata*
Exposed to Corpus Christi Sediment at 30‰S

Tissue Cr then dropped to 7 mg/kg on day 32. The controls showed only a moderate increase in tissue Cr levels from 4.1 mg/kg on day 0 to 5 mg/kg on day 20. The lack of significance of the results is undoubtedly attributable to the large standard deviations measured in the exposed samples.

144. *Palaemonetes pugio*. Exposure, time, salinity, and the interactions of exposure:salinity contributed significantly to the accumulation of Cr by the shrimp *P. pugio* exposed to Texas City sediment at 15‰ and 30‰. However, at 30‰ there was little variation in the concentration of Cr in control and exposed animals, with the range of means extending from less than 0.2 mg/kg to 0.4 mg/kg (Figure 108). Both control and exposed animals behaved similarly. At 15‰, on the other hand, there was a significant increase with time in the concentration of Cr in exposed shrimp from 12. mg/kg on day 2 to 3.7 mg/kg on day 32 (Figure 109). Chromium concentrations in the controls remained at or below the detection limit of 0.5 mg/kg at all sampling times. Thus significant uptake of Cr from the sediment occurred only at 15‰.

145. *P. pugio* exposed to Corpus Christi sediment at 15‰ and 30‰ failed to show a significant accumulation of chromium. However, salinity did significantly affect the concentrations of Cr measured. This may have been an artifact of sample size, since measured mean tissue Cr concentrations ranged from 0.05 mg/kg to 0.62 mg/kg at 15‰, while at 30‰ values were below the detection limit of 1.0 mg/kg indicating inadequate sample sizes in this experiment (Figures 110 and 111).

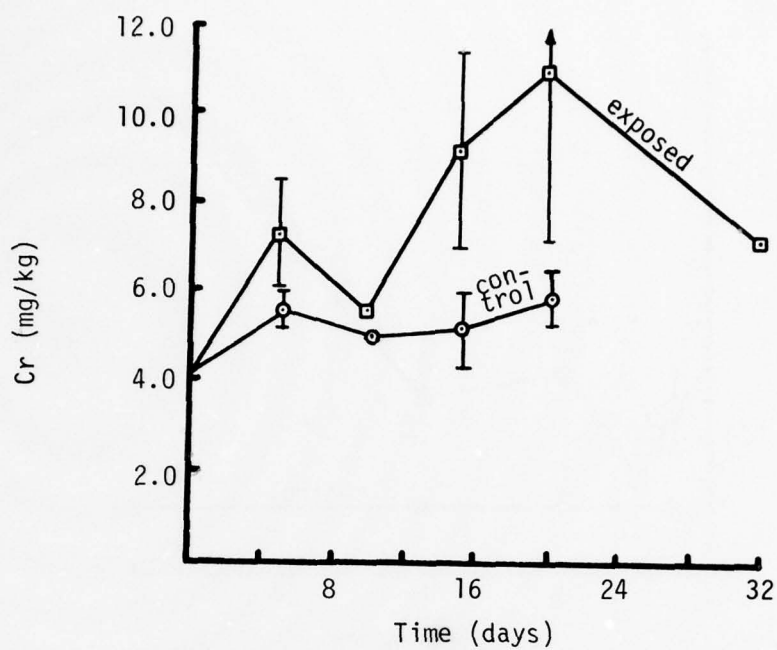


Figure 107. Mean Cr Uptake by *Rangia cuneata*
Exposed to Ashtabula Sediment in fresh water

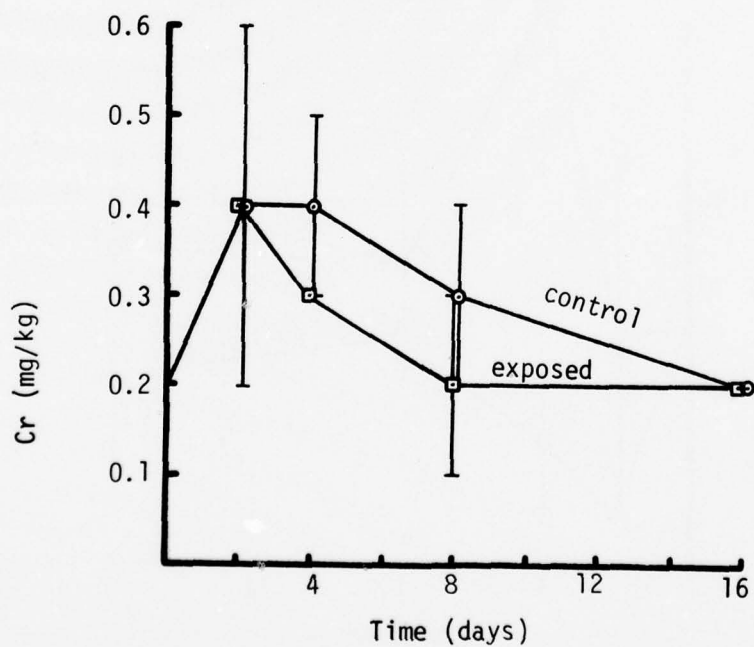


Figure 108. Mean Cr Uptake by *Palaemonetes pugio*
Exposed to Texas City Sediment at 30‰S

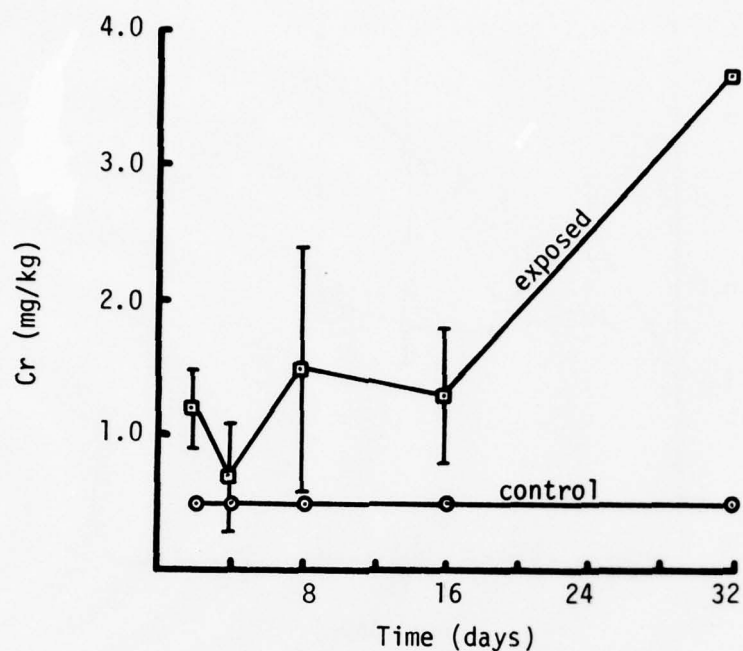


Figure 109. Mean Cr Uptake by *Palaemonetes pugio* Exposed to Texas City Sediment at 15‰S

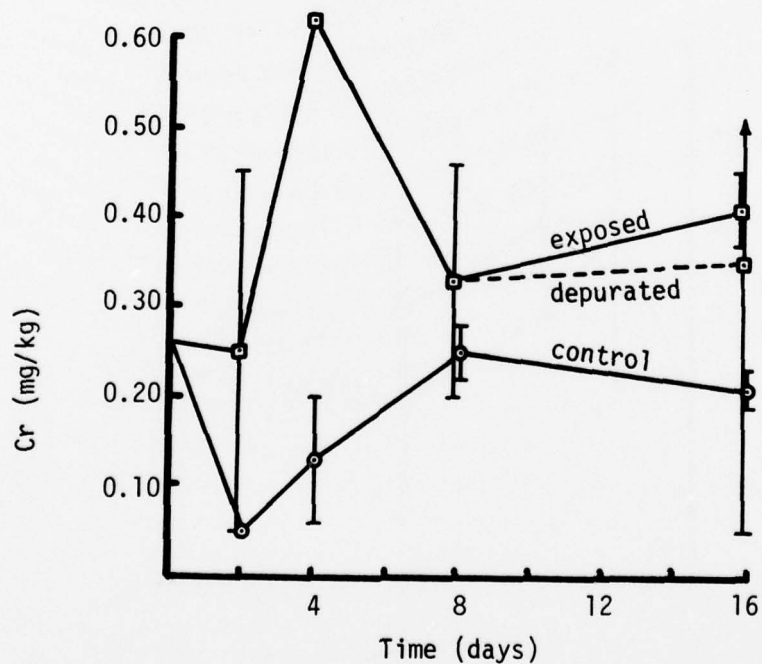


Figure 110. Mean Cr Uptake by *Palaemonetes pugio* Exposed to Corpus Christi Sediment at 15‰S

146. *Palaemonetes kadiakensis*. Neither time nor exposure contributed significantly to Cr uptake by *P. kadiakensis* exposed to Ashtabula sediment in fresh water. Chromium concentrations were similar in control and exposed shrimp and fell in the range of 1.3 mg/kg to 4.1 mg/kg between days 0 and 20 of the experiment (Figure 112). At the day 32 sampling time, the Cr concentration in the exposed shrimp rose to 11.2 mg/kg. Unfortunately, a control sample was not available at this time.

147. *Neanthes arenaceodentata*. Both time and exposure made highly significant contributions to the accumulation of Cr from Texas City sediment at 30‰ by the worm *N. arenaceodentata*. Chromium concentrations in exposed worms were significantly higher than those in control worms at all sampling times (Figure 113). In the former, Cr concentrations rose from less than 1 mg/kg on day 0 to a mean of 5.8 mg/kg on day 32. Chromium levels in the controls rose from less than 1 mg/kg on day 16 to a mean of 3.8 mg/kg on day 32. There was a drop in Cr concentration from 3.2 mg/kg to 1.6 mg/kg in animals exposed to sediment for 8 days and then allowed to depurate for 8 days.

148. The two experiments in which *N. arenaceodentata* were exposed to Corpus Christi sediment at 30‰ yielded roughly similar results. Exposure and time did not contribute to Cr uptake by the worms in either experiment. In both experiments, Cr levels in control and exposed worms showed erratic fluctuations, with the range of variation being greater in the first experiment than the second (Figures 114 and 115).

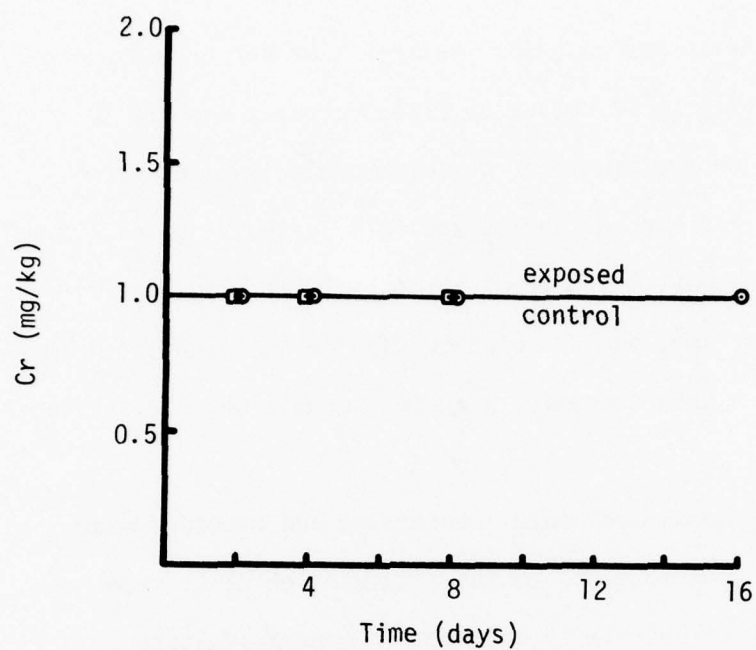


Figure 111. Mean Cr Uptake by *Palaemonetes pugio*
Exposed to Corpus Christi Sediment at 30‰S

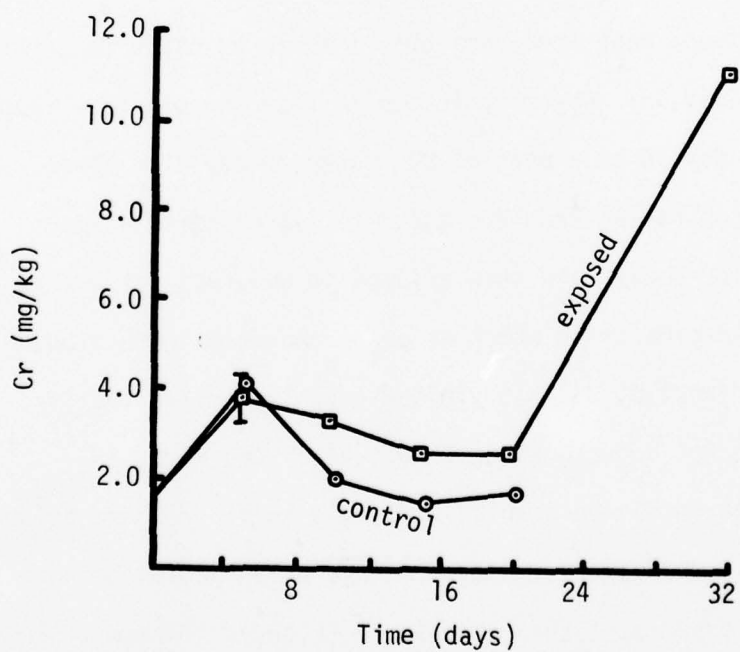


Figure 112. Mean Cr Uptake by *Palaemonetes kadia-*
kensis Exposed to Asthabula Sediment in fresh water

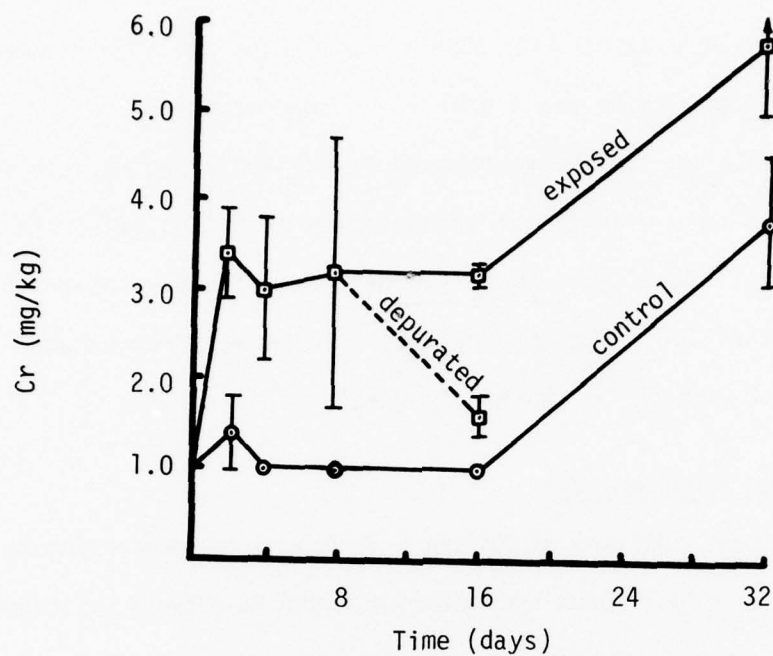


Figure 113. Mean Cr Uptake by *Neanthes arenaceodentata*
Exposed to Texas City Sediment at 30‰

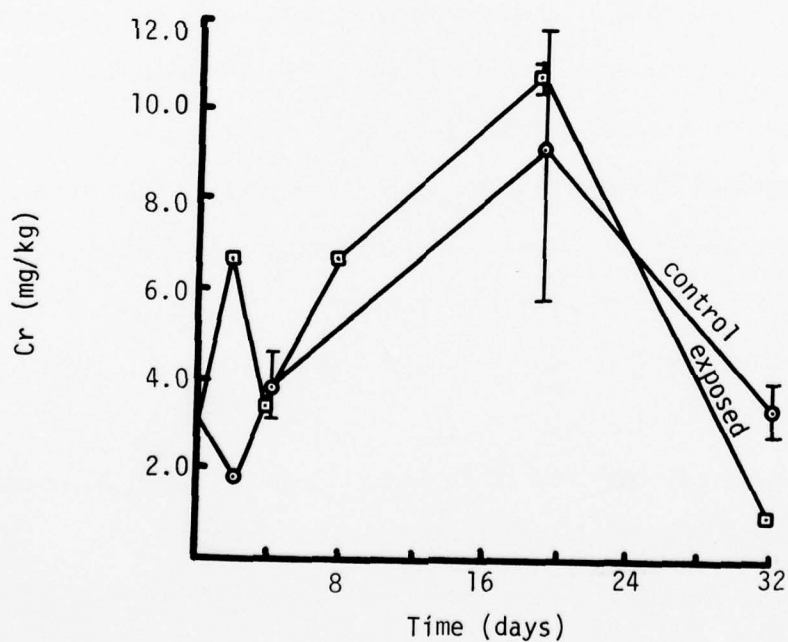


Figure 114. Mean Cr Uptake by *Neanthes arenaceodentata*
Exposed to Corpus Christi Sediment at 30‰
[First Run]

In animals which were exposed to sediment for 8 days and then allowed to depurate for 8 days, there was a drop in Cr concentrations.

149. *Tubifex* sp. that were exposed to Ashtabula sediment in fresh water failed to show a significant accumulation of Cr due either to exposure or time. Only two samples yielded concentrations above the detection limit of 1.0 mg/kg (Figure 116). These were for exposed animals on day 2 and day 32 (both 2.0 mg/kg).

Mercury (Hg) and Vanadium (V)

150. The only analyses of Hg and V in the short-term exposure studies for which significant accumulation might have been indicated were those performed on *Rangia cuneata* and *Palaemonetes kadiakensis* exposed to the Ashtabula sediment in fresh water. Analyses of *R. cuneata*, *P. pugio*, and *N. arenaceodentata* exposed to both Texas City and Corpus Christi sediments at 15‰ and 30‰ showed Hg levels in both control and exposed animals to be at or below detection limits. On several occasions, single samples slightly exceeded these levels but such occurrences were randomly distributed between control and exposed organisms. For this reason, statistical analyses of Hg for short-term studies involving Corpus Christi or Texas City sediment were not possible.

151. Statistical analyses of Hg and V accumulation by *R. cuneata* and *P. kadiakensis* are summarized in Tables A9 and A10.

152. *Rangia cuneata*. Statistical analysis indicated that exposure and time did not have a significant effect on Hg uptake by *R. cuneata*.

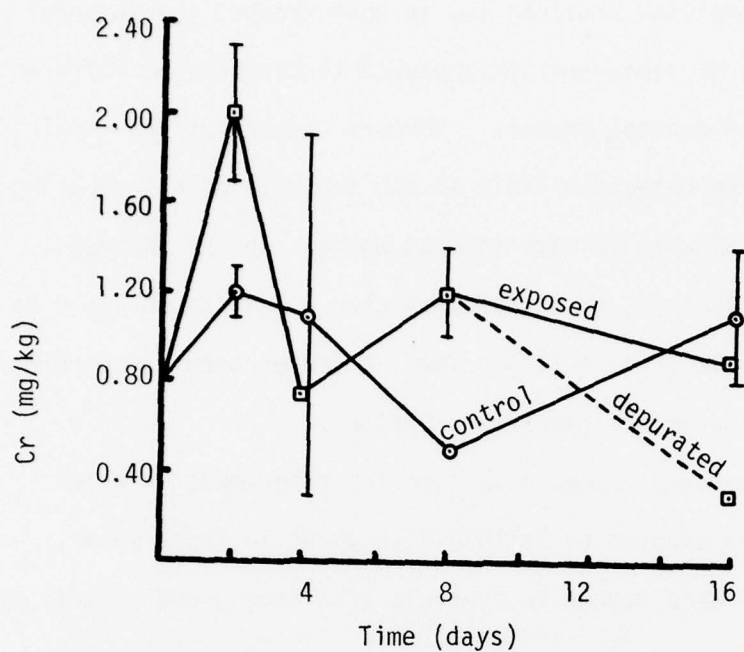


Figure 115. Mean Cr Uptake by *Nereis arenaceodentata*
Exposed to Corpus Christi Sediment at 30‰S
[Second Run]

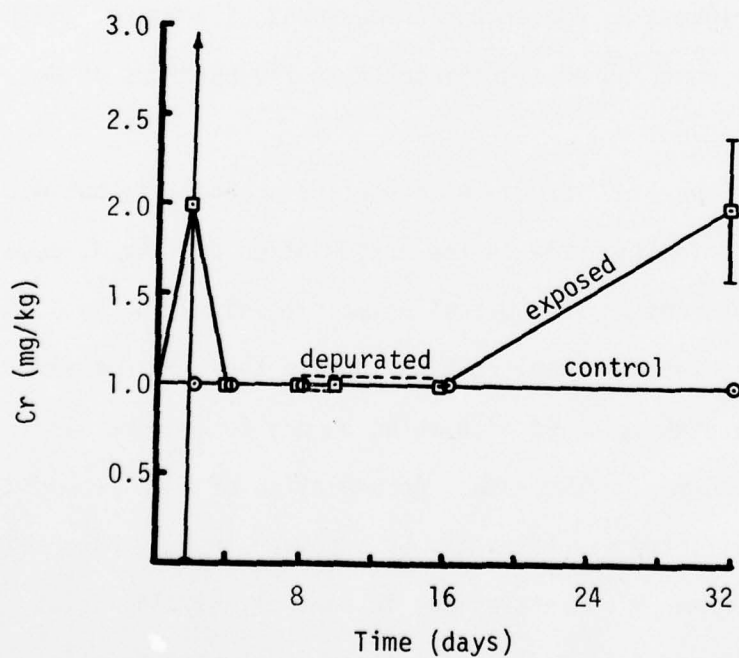


Figure 116. Mean Cr Uptake by *Tubifex* sp. Exposed to
Ashtabula Sediment in fresh water

Though Hg concentrations remained low in both groups, the temporal pattern of tissue Hg concentration appeared to be somewhat different in the exposed and control animals. Mercury concentrations remained below the 0.2 mg/kg detection limit in the controls at all sampling times except day 32 when it rose to 0.38 mg/kg. In the exposed animals, Hg concentrations rose from less than 0.2 mg/kg on day 0 to 0.75 mg/kg on day 32 (Figure 117). Thus, a longer term exposure might show significant Hg uptake (see next section).

153. *Palaemonetes kadiakensis*. In the experiment in which *P. kadiakensis* was exposed to Ashtabula sediment in fresh water, Hg concentrations were higher in controls than in exposed animals at all sampling times for which both a control and an exposed sample were available (Figure 118). The single sample of 32-day exposed animals had the highest Hg concentration measured, 6.4 mg/kg. Neither exposure nor time contributed significantly to the patterns of Hg concentration observed.

154. *Rangia cuneata*. Exposure to Ashtabula sediment, but not time, contributed significantly to the accumulation of V by *R. cuneata*. Vanadium concentrations in the control animals remained in the 0.36 mg/kg to 0.66 mg/kg range at all sampling times, while those in exposed animals reached a peak value of 11.8 mg/kg on day 20 (Figure 119).

155. *Palaemonetes kadiakensis*. Accumulation of V by *P. kadiakensis* was also affected significantly by exposure to Ashtabula sediment but not by time. Mean V concentrations in control animals varied between 0.31 mg/kg and 0.56 mg/kg while those in exposed animals

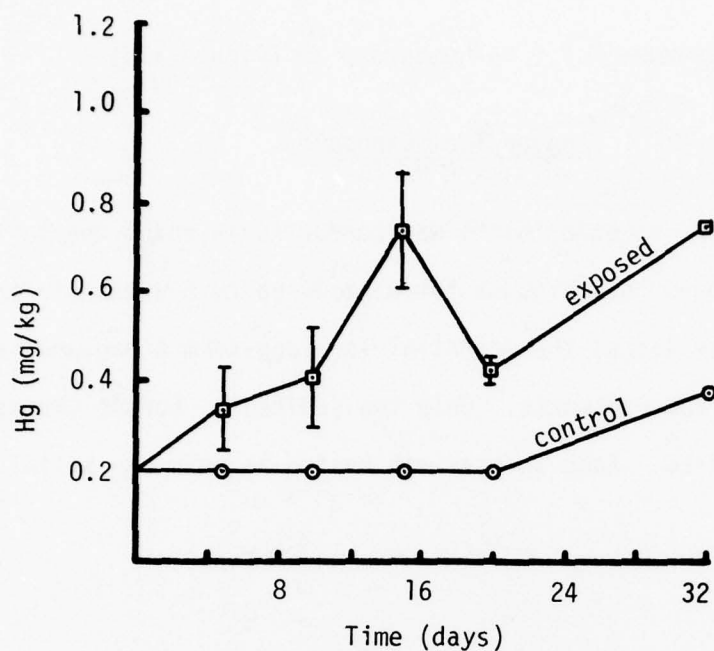


Figure 117. Mean Hg Uptake by *Rangia cuneata* Exposed to Ashtabula Sediment in fresh water

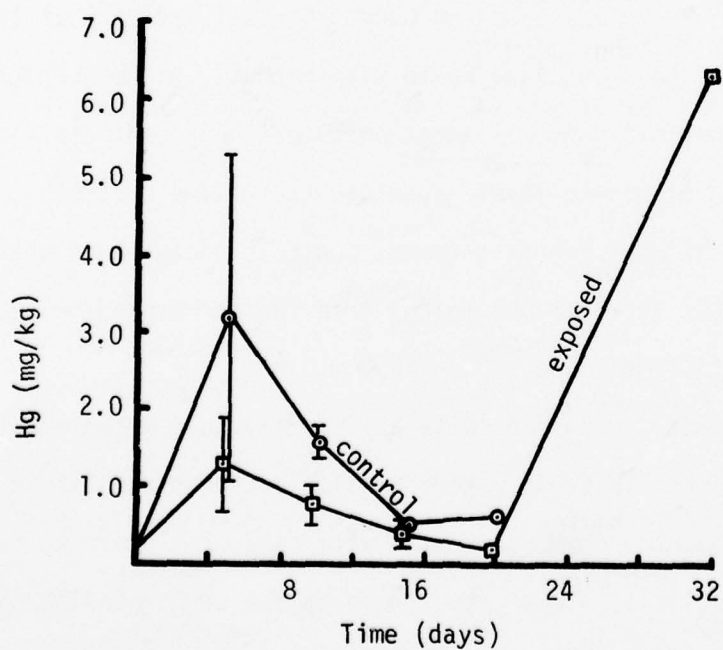


Figure 118. Mean Hg Uptake by *Palaemonetes kadiakensis* Exposed to Ashtabula Sediment in fresh water

increased to a maximum of 1.9 mg/kg on day 20 (Figure 120).

Longer Term Exposures

156. A series of experiments was conducted in which the test animals were exposed to sediments for periods up to 6 weeks in order to more completely assess the potential for long-term bioaccumulation of heavy metals from sediments. Only two sediments, Corpus Christi and Ashtabula, were used. Each species was tested at only one salinity in each sediment.

Iron (Fe)

157. Statistical analyses of Fe accumulation by all species in the longer term exposures are summarized in Table A11.

158. *Rangia cuneata* exposed to Corpus Christi sediment at 15‰S for 6 weeks failed to accumulate Fe to significantly higher concentrations than did controls. At all sampling times, both controls and experimentals had higher Fe levels than did the 0-time controls (296 mg/kg Fe). At most sampling times, controls contained higher Fe concentrations (506 mg/kg to 682 mg/kg) than the corresponding sediment-exposed animals (351 mg/kg to 528 mg/kg).

159. *R. cuneata* responded quite differently to 6 weeks exposure to Ashtabula sediment in fresh water. While Fe concentrations in both the control and exposed clams increased with time, Fe levels in exposed clams were substantially higher than those in the corresponding control animals at all sampling times (Figure 121). Iron concentrations in

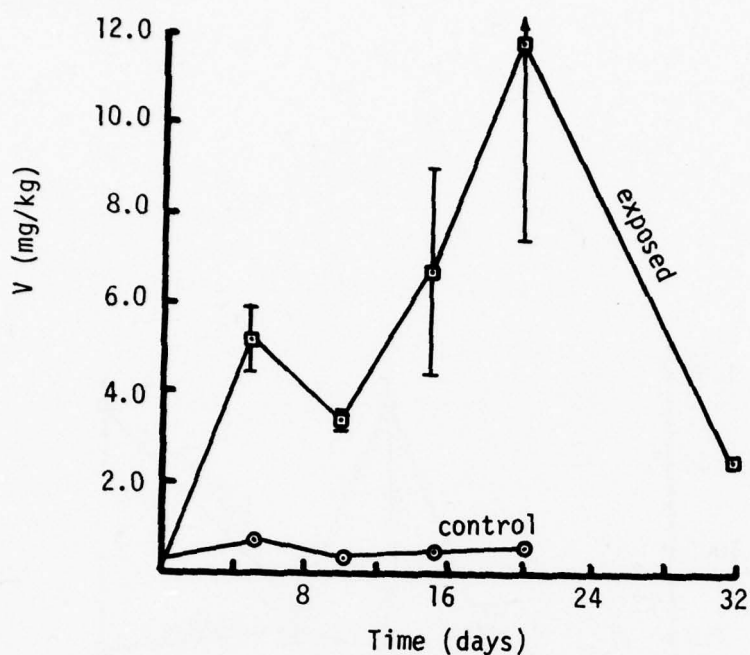


Figure 119. Mean V Uptake by *Rangia cuneata* Exposed to Ashtabula Sediment in fresh water

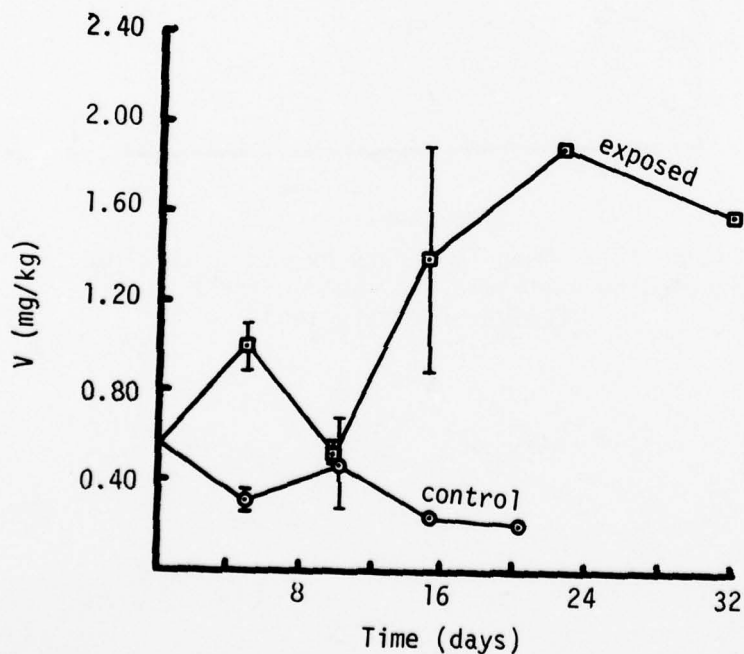


Figure 120. Mean V Uptake by *Palaemonetes kadiakensis* Exposed to Ashtabula Sediment in fresh water

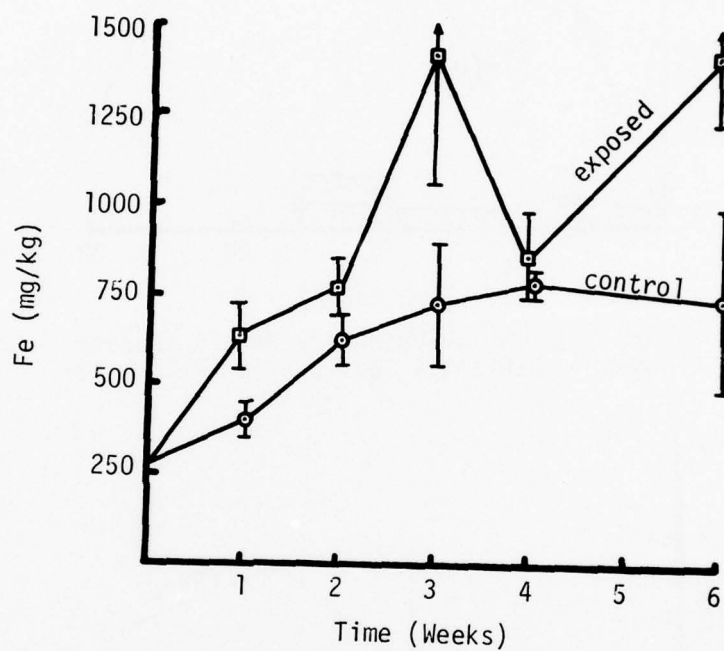


Figure 121. Mean Fe Uptake by *Rangia cuneata*
Exposed to Ashtabula Sediment in fresh water
[Longer Term Studies]

exposed animals rose from a mean of 279 mg/kg on day 0 to 1422 mg/kg at 6 weeks while the Fe concentrations in the controls rose only to 745 mg/kg in the same time period. Exposure, time, and their interaction contributed significantly to the results obtained.

160. *Palaemonetes pugio*. Control shrimp, *P. pugio*, and those exposed to Corpus Christi sediment at 15‰ showed variable levels of tissue Fe during the 6-week experiment (Figure 122). Iron levels were higher in the controls than in the corresponding exposed animals at 3 of the 5 sampling times. Statistical analysis revealed that exposure, time, and their interaction contributed significantly to the patterns of tissue Fe recorded. However, in this case the effect of exposure to sediment was inverse.

161. *Palaemonetes kadiakensis* showed a significant accumulation of Fe from Ashtabula sediment in fresh water during 6 weeks exposure. At all sampling times, Fe concentrations in exposed animals were significantly higher than those in the controls and reached a maximum of 409 mg/kg at the 2-week sampling time (Figure 123). Mean Fe concentrations in control animals varied between 40 mg/kg and 91.6 mg/kg and showed a rising trend during the time course of the experiment.

162. *Neanthes arenaceodentata* exposed to Corpus Christi sediment at 30‰ showed an increase in tissue Fe concentrations from a day-0 value of 110 mg/kg to 481 mg/kg and 374 mg/kg after 3 and 4 weeks, respectively. However, regression analysis showed that Fe accumulation was not significantly affected by exposure, time, or their interaction. This was due to the fact that during the same 4-week exposure

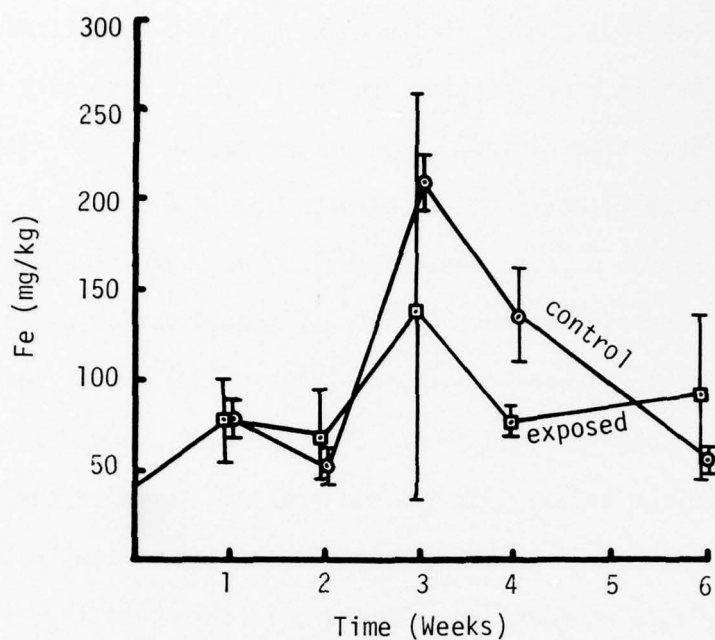


Figure 122. Mean Fe Uptake by *Palaemonetes pugio*
Exposed to Corpus Christi Sediment at 15‰S
[Longer Term Studies]

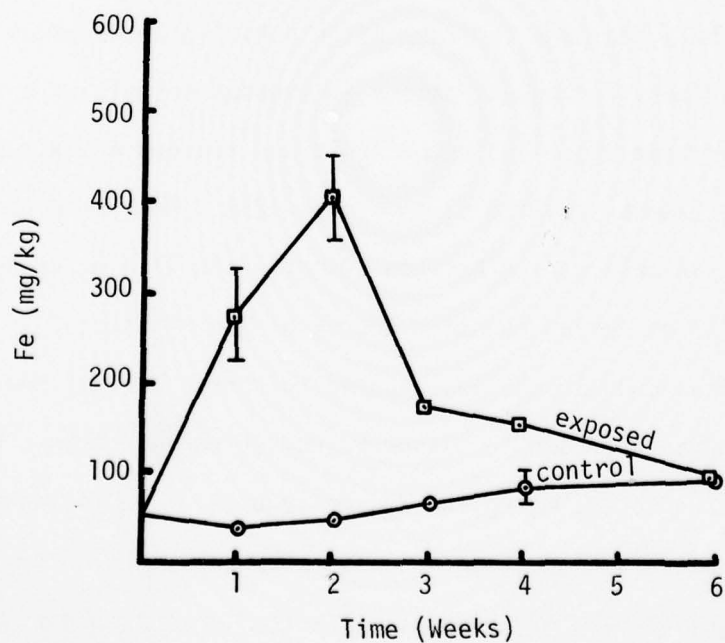


Figure 123. Mean Fe Uptake by *Palaemonetes kadiakensis*
Exposed to Ashtabula Sediment in fresh water
[Longer Term Studies]

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TEXAS A AND M RESEARCH FOUNDATION COLLEGE STATION

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AVAILABILITY OF SEDIMENT-ADSORBED HEAVY METALS TO BENTHOS WITH --ETC(U)

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period, Fe concentrations in control animals rose in a similar fashion to 348 mg/kg.

163. *Tubifex* sp. Iron concentrations were quite high at all sampling times in control *Tubifex* sp. and in worms exposed to Ashtabula sediment in fresh water for six weeks. However, tissue Fe levels in exposed animals rose from a 0-day value of 532 mg/kg to 1231 mg/kg at 3 weeks and 993 mg/kg at 6 weeks, while Fe concentrations in controls rose only to 823 mg/kg (Figure 124). Both main effects, but not their interaction, were significant.

Manganese (Mn)

164. Statistical analyses of Mn accumulation by all species in longer term exposures are summarized in Table A12.

165. *Rangia cuneata* failed to accumulate Mn from Corpus Christi sediment at 15°/°S. Manganese concentrations in exposed animals varied between 36 mg/kg and 45 mg/kg, while those in controls rose steadily from 22 mg/kg at 1 week to 74 mg/kg at 4 weeks. Neither of the main effects or their interaction were significant.

166. *R. cuneata* also failed to accumulate Mn from Ashtabula sediment in fresh water. Manganese concentrations were more variable in these animals. They varied irregularly from 43.6 mg/kg to 75.6 mg/kg in exposed animals and from 27 mg/kg to 124 mg/kg in controls, while the 0-day animals contained a mean of 19.5 mg/kg Mn (Figure 125). Exposure was without significant effect on the levels of Mn observed. However, time and the interaction of exposure and time were significant, undoubtedly reflecting the temporal rising trend in tissue Mn concentrations in the control animals.

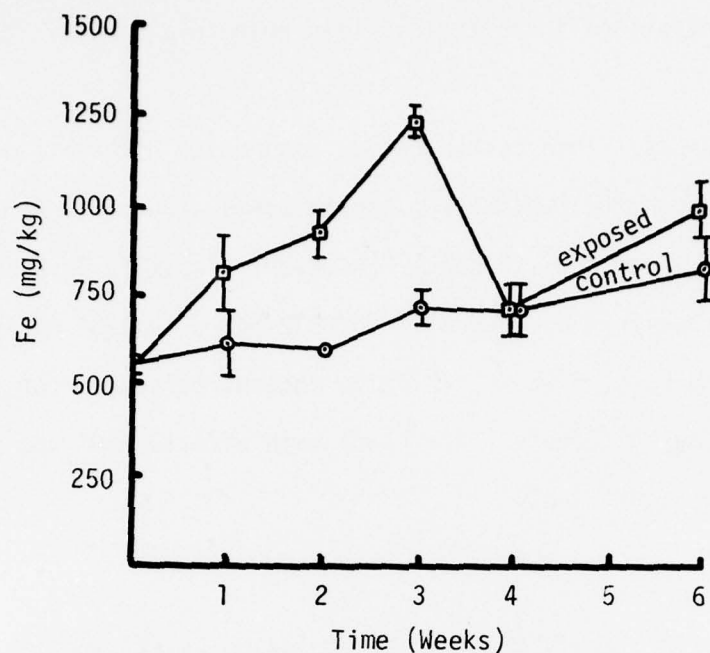


Figure 124. Mean Fe Uptake by *Tubifex* sp.
Exposed to Ashtabula Sediment in fresh water
[Longer Term Studies]

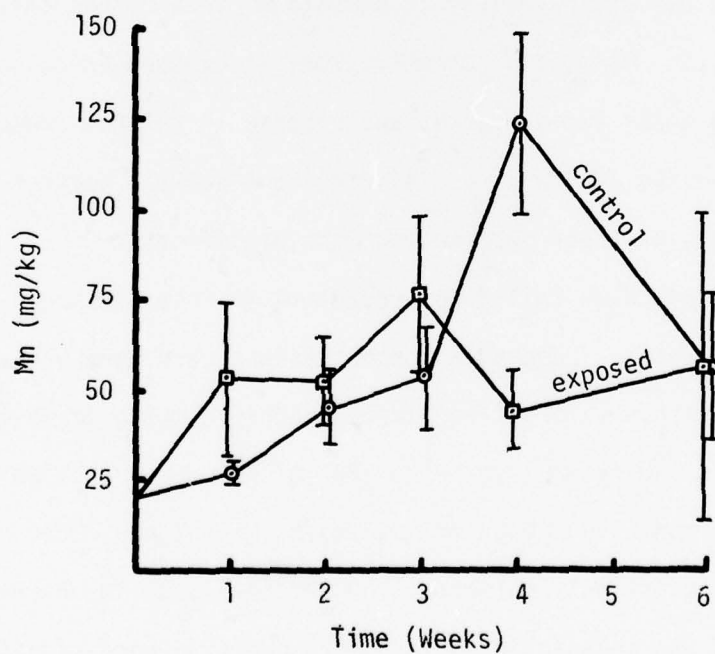


Figure 125. Mean Mn Uptake by *Rangia cuneata*
Exposed to Ashtabula Sediment in fresh water
[Longer Term Studies]

167. *Palaemonetes pugio*. Exposure and the interaction of exposure and time were without significant effect on the accumulation of Mn by *P. pugio* during 6 weeks exposure to Corpus Christi sediment at 15‰. However, the main effect of time was significant. In both the control and exposed groups, Mn concentrations increased with time from a 0-day value of 9.3 mg/kg to 17 mg/kg at 4 weeks in the exposed group and 19 mg/kg to 18.9 mg/kg at weeks 3 and 4 in the controls.

168. *Palaemonetes kadiakensis*. Regression analysis revealed that exposure, time, and their interaction all contributed in a highly significant fashion to the accumulation of Mn from Ashtabula sediment in fresh water by the shrimp *P. kadiakensis*. Manganese concentrations in exposed animals rose from a day-0 value of 12.8 mg/kg to 36.4 mg/kg at 2 weeks and then dropped gradually to 14.1 mg/kg at 6 weeks. On the other hand, in the controls, mean Mn concentrations rose more gradually to 18.9 mg/kg at 4 weeks and then dropped to 16.5 mg/kg at 6 weeks.

169. *Neanthes arenaceodentata*. Exposure, but not time or the interaction of exposure and time, contributed significantly to the accumulation of Mn from Corpus Christi sediment in 30‰ seawater by *N. arenaceodentata*. Manganese concentrations in exposed animals rose from 9.5 mg/kg at 1 week to 17 mg/kg at 4 weeks, while those in controls varied irregularly between 7.3 mg/kg and 11.3 mg/kg (Figure 126).

170. *Tubifex* sp. did not show a significant accumulation of Mn during 6 weeks exposure to Ashtabula sediment in fresh water. Manganese

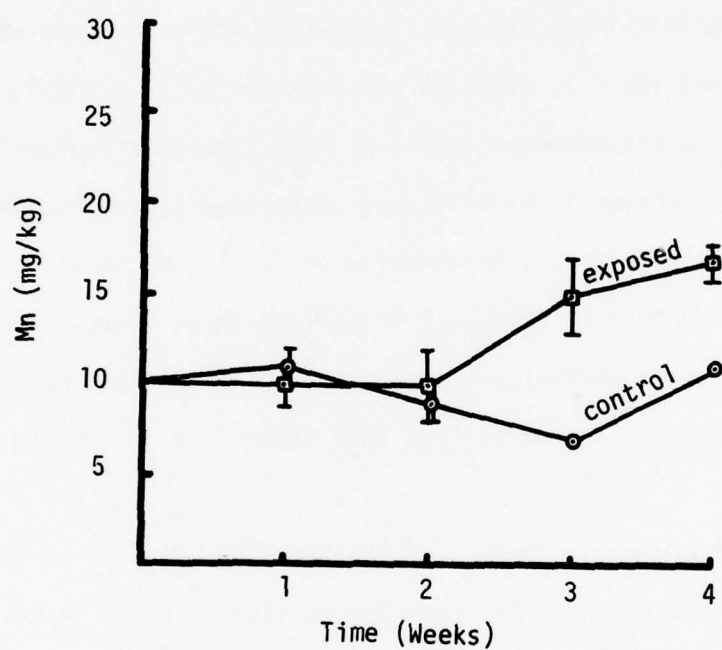


Figure 126. Mean Mn Uptake by *Neanthes arenaceodentata*
Exposed to Corpus Christi Sediment at 30‰ S
[Longer Term Studies]

concentrations varied from 13.5 mg/kg to 22.5 mg/kg in exposed animals and from 11 mg/kg to 20 mg/kg in control animals during the time course of the experiment.

Copper (Cu)

171. Statistical analyses of Cu accumulation by all species during longer term exposures are summarized in Table A13.

172. *Rangia cuneata*. The 0-day control clams from the population used in the 6-week exposure to Corpus Christi sediment at 15‰ contained a mean of 22 mg/kg copper. Mean Cu concentrations in both control and exposed animals were lower than this at all subsequent sampling times and varied between 10 mg/kg and 17 mg/kg. Both main effects and their interaction were not significant.

173. Concentrations of Cu in control *R. cuneata* and in clams exposed to Ashtabula sediment in fresh water were almost identical at all sampling times. At each sampling time, mean Cu concentrations in the two groups differed by less than 1 mg/kg and rose gradually from 11.8 mg/kg at day 0 to 16.2 mg/kg and 16.4 mg/kg after 6 weeks in the exposed and control clams, respectively. Exposure, time, and their interaction were not significant.

174. *Palaemonetes pugio*. Exposure and time, but not their interaction, were found to contribute significantly to the levels of Cu measured in the tissues of *P. pugio* during 6 weeks exposure to Corpus Christi sediment at 15‰. However, at all but the 6-week sampling time, Cu concentrations in control animals were higher than

those in sediment-exposed shrimp. At 6 weeks, control and exposed animals contained similar concentrations of Cu, 55.7 mg/kg and 56.3 mg/kg, respectively. Thus, the significant effect of exposure was inverse.

175. *Palaemonetes kadiakensis*. Exposure and time, but not their interaction, were also found to contribute significantly to the levels of Cu measured in the tissues of *P. kadiakensis* during 6 weeks exposure to Ashtabula sediment in fresh water. However, in this case, Cu concentrations in exposed animals were higher than those in the corresponding controls at all sampling times (Figure 127). Mean Cu concentrations reached a maximum of 118 mg/kg in the exposed animals and 103 mg/kg in the controls at 2 weeks and then declined slightly to 106 mg/kg and 89 mg/kg, respectively, at 6 weeks.

176. *Neanthes arenaceodentata* failed to show a significant accumulation of Cu from Corpus Christi sediment at 30‰ during four weeks exposure. Mean Cu concentrations in control and exposed animals were similar at all sampling times and decreased gradually from 44 mg/kg to 28 mg/kg during the time course of the experiment.

177. *Tubifex* sp. also failed to accumulate significant amounts of Cu from Ashtabula sediment in fresh water. During the exposure period, Cu concentrations in the exposed and control animals varied between 9 mg/kg and 19 mg/kg, while the 0-time controls contained a mean of 7 mg/kg copper.

Cadmium (Cd)

178. Statistical analyses of Cd accumulation by all species in longer term exposures are summarized in Table A14.

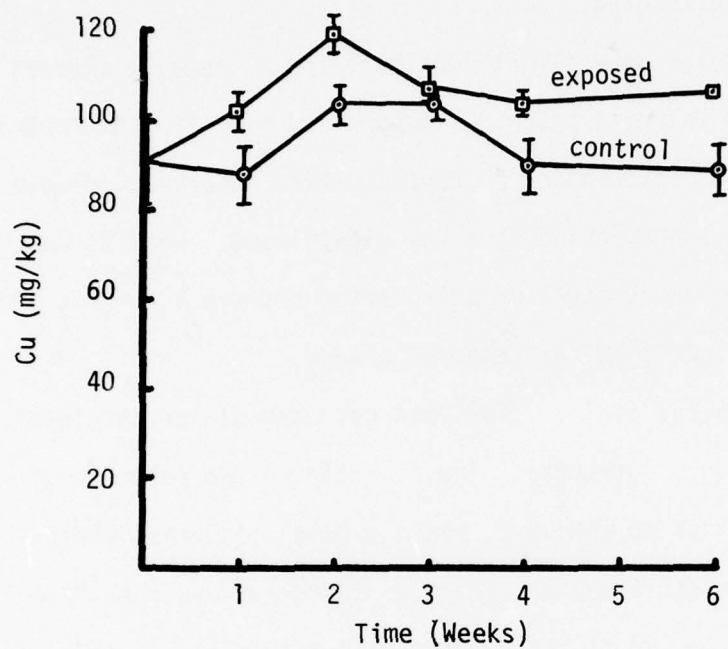


Figure 127. Mean Cu Uptake by *Palaemonetes kadiakensis*
Exposed to Ashtabula Sediment in fresh water
[Longer Term Studies]

179. *Rangia cuneata* failed to accumulate Cd during 6 weeks exposure to Corpus Christi sediment at 15‰. Mean Cd concentrations in control and exposed animals showed very little temporal variation and ranged from 1.3 mg/kg to 2.7 kg/kg.

180. The results were almost identical for *R. cuneata* exposed to Ashtabula sediment in fresh water. Exposure and time did not contribute significantly to the patterns of Cd concentration observed. However, the interaction of exposure and time was significant. Mean Cd concentrations in exposed and control animals varied between 1.0 mg/kg and 3 mg/kg, with no clear trend of temporal change.

181. *Palaemonetes pugio*. Time, but not exposure or the interaction of exposure and time, contributed significantly to the patterns of tissue Cd distribution in shrimp *P. pugio* exposed to Corpus Christi sediment at 15‰ for 6 weeks. Mean Cd concentrations rose from a 0-day value of 0.07 mg/kg to the range of 0.21 mg/kg to 0.51 mg/kg in controls and 0.22 mg/kg to 0.30 mg/kg in exposed animals during the time course of the experiment. This accounts for the statistical results.

182. *Palaemonetes kadiakensis* accumulated Cd from Ashtabula sediment in fresh water. Exposure, time, and their interaction were significant. Mean Cd concentrations in exposed animals rose from a day-0 value of 0.28 mg/kg to 0.37 mg/kg at two weeks and then fell gradually to 0.21 mg/kg at six weeks (Figure 128). Cadmium concentrations in controls varied only slightly between 0.17 mg/kg and 0.22 mg/kg.

183. *Neanthes arenaceodentata* failed to accumulate Cd from

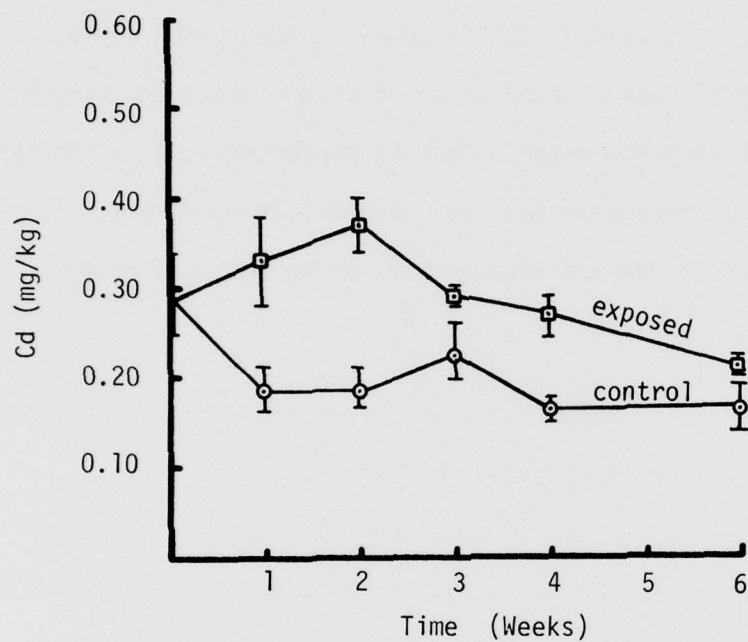


Figure 128. Mean Cd Uptake by *Palaemonetes kadiakensis*
Exposed to Ashtabula Sediment in fresh water
[Longer Term Studies]

Corpus Christi sediment at 30‰. From a 0-day value of 2.2 mg/kg, Cd concentrations in exposed animals rose gradually to 3.2 mg/kg at 4 weeks, while in the controls, Cd concentrations rose to 3.0 mg/kg in the same time period.

184. *Tubifex* sp. Time, but not exposure or the interaction of exposure and time, contributed significantly to the levels of Cd determined in the tissues of *Tubifex* sp. during 6 weeks exposure to Ashtabula sediment in fresh water. Mean Cd concentrations in exposed animals varied in an irregular fashion between 0.29 mg/kg and 0.49 mg/kg, while those in controls varied between 0.21 mg/kg and 0.63 mg/kg.

Nickel (Ni)

185. Statistical analyses of Ni accumulation by all species in longer term exposures are summarized in Table A15.

186. *Rangia cuneata*. At all sampling times during the longer term experiments, mean Ni concentrations were below the day-0 value of 30 mg/kg in the tissues of control *R. cuneata* and clams exposed to Corpus Christi sediment at 15‰ for 6 weeks. Nickel concentrations in exposed animals varied between 14 mg/kg and 19 mg/kg while those in controls varied between 17 mg/kg and 26 mg/kg. Exposure, time, and their interaction were not significant.

187. However, *R. cuneata* exposed to Ashtabula sediment in fresh water showed a significant uptake of nickel. Time and the interaction of exposure and time were also significant. Mean Ni concentrations in exposed animals rose from a day-0 value of 14.5 mg/kg to 36 mg/kg at 6 weeks (Figure 129). In the controls, Ni concentrations rose to a peak

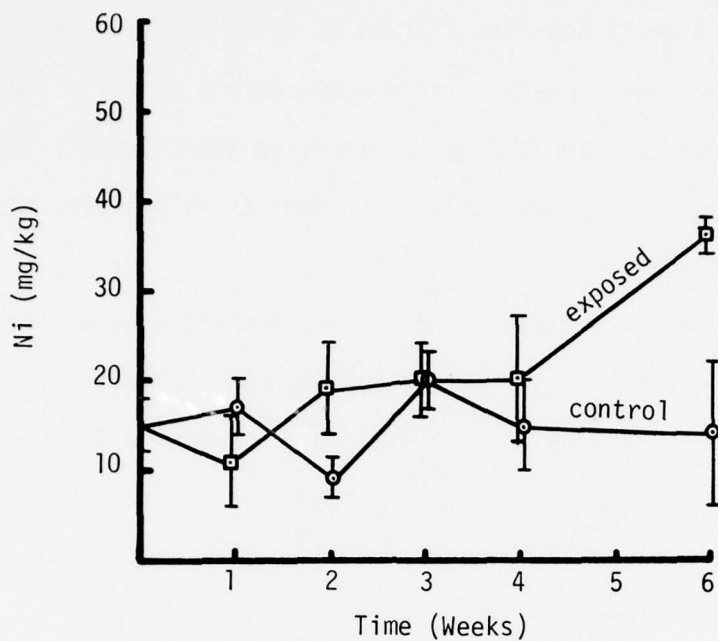


Figure 129. Mean Ni Uptake by *Rangia cuneata* Exposed to Ashtabula Sediment in fresh water [Longer Term Studies]

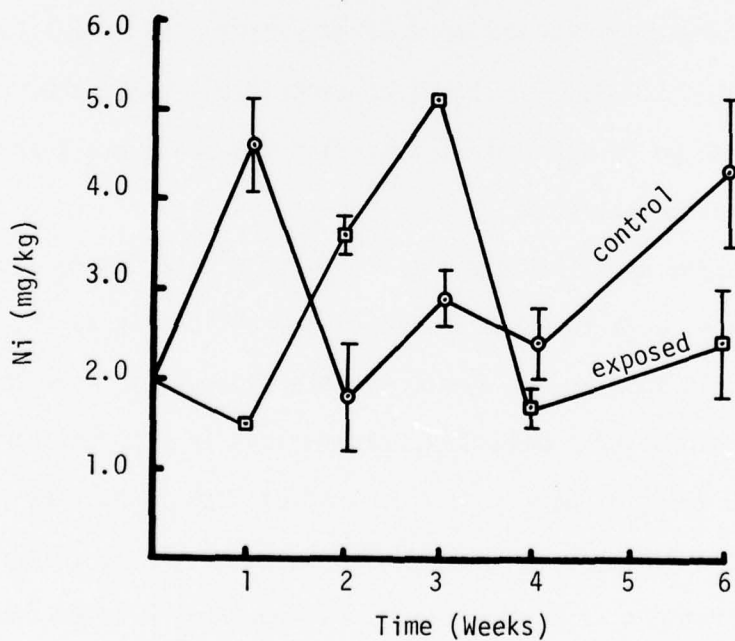


Figure 130. Mean Ni Uptake by *Tubifex* sp. Exposed to Ashtabula Sediment in fresh water [Longer Term Studies]

of 20 mg/kg at 3 weeks and then dropped to 14 mg/kg at 6 weeks.

188. *Palaemonetes pugio*. The concentrations of Ni in the tissues of *P. pugio* were below the 0.7 mg/kg detection limit in controls and in animals exposed to Corpus Christi sediment at 15‰ for 6 weeks at all sampling times.

189. *Palaemonetes kadiakensis*. Time, but not exposure or the interaction of exposure and time, contributed significantly to the pattern of Ni distribution in *P. kadiakensis* exposed to Ashtabula sediment in fresh water for 6 weeks. Mean Ni concentrations rose to a peak of 2.3 mg/kg in exposed animals and 1.7 mg/kg in controls at 3 weeks and then dropped to lower values at 5 and 6 weeks.

190. *Neanthes arenaceodentata*. Neither of the main effects or their interaction contributed significantly to the concentrations of Ni found in *N. arenaceodentata* during 4 weeks exposure to Corpus Christi sediment at 30‰. Mean tissue Ni concentrations were below the 0-day value of 14.8 mg/kg in both the controls and exposed animals at all subsequent sampling times.

191. *Tubifex sp.* Time and the interaction of exposure and time, but not exposure, were found to contribute significantly to the levels of Ni measured in *Tubifex sp.* during 6 weeks exposure to Ashtabula sediment in fresh water. Mean Ni concentrations in exposed animals rose from 1.45 mg/kg at week 1 to 5.1 mg/kg at week 3 and then dropped to 1.6 mg/kg and 2.4 mg/kg at weeks 4 and 6, respectively (Figure 130). Nickel concentrations in controls varied irregularly between 1.8 mg/kg and 4.6 mg/kg during the same time period and were higher than those in

exposed animals at weeks 1, 4, and 6.

Lead (Pb)

192. Statistical analyses of Pb accumulation by all species during longer term exposures are summarized in Table A16.

193. *Rangia cuneata*. The main effects of exposure and time as well as their interaction did not contribute significantly to the accumulation of Pb from Corpus Christi sediment at 15‰ by *R. cuneata*. Mean Pb concentrations in exposed animals decreased from an initial value of 1.15 mg/kg to 0.4 mg/kg at 6 weeks. Lead concentrations in controls varied between 0.2 mg/kg and 1.6 mg/kg.

194. Mean Pb concentrations in *R. cuneata* also dropped during 6 weeks exposure to Ashtabula sediment in fresh water. The mean day-0 Pb concentration in the clams was 2.3 mg/kg, and Pb concentrations in control and exposed animals varied between 0.36 mg/kg and 2.16 mg/kg at all subsequent sampling times. Exposure, time, and their interaction were not significant.

195. *Palaemonetes pugio* contained low and only slightly variable concentrations of Pb during 6 weeks exposure to Corpus Christi sediment at 15‰. Mean Pb concentrations in exposed animals varied between 0.09 mg/kg and 0.31 mg/kg and those in the controls varied between 0.14 mg/kg and 0.20 mg/kg during the time course of the experiment. Exposure, time, and their interaction were not significant.

196. *Palaemonetes kadiakensis*. Exposure was significant ($P > F = 0.03$) while time and the interaction of exposure and time were not significant in the accumulation of Pb by *P. kadiakensis* during 6 weeks

exposure to Ashtabula sediment in fresh water. However, the differences in Pb concentrations in control and exposed animals were small. Mean Pb concentrations in exposed animals rose from a day-0 value of 0.52 mg/kg to 2 peaks of 0.67 mg/kg and 0.63 mg/kg at 2 and 6 weeks, respectively. Mean Pb concentrations in controls varied only slightly between 0.36 mg/kg and 0.43 mg/kg during the same time period.

197. *Neanthes arenaceodentata*. Exposure, time, and their interaction did not contribute significantly to the accumulation of Pb by *N. arenaceodentata* during 4 weeks exposure to Corpus Christi sediment at 30°/°S. Mean Pb concentrations in exposed and control animals varied between 1.2 mg/kg and 2.2 mg/kg and were below the day-0 value of 1.9 mg/kg at all but one sampling time.

198. *Tubifex sp.* Time, but not exposure or the interaction of exposure and time, contributed significantly to the pattern of Pb concentrations measured in *Tubifex sp.* during 6 weeks exposure to Ashtabula sediment in fresh water. Lead concentrations were higher in these animals than in any others and varied between 3.6 mg/kg and 12.2 mg/kg in exposed animals and 4.7 mg/kg and 8.8 mg/kg in controls. There was a trend among both control and exposed animals for Pb concentrations to increase with time (Figure 131).

Zinc (Zn)

199. Statistical analyses of Zn accumulation by all species during longer term exposures are summarized in Table A17.

200. *Rangia cuneata*. There was very little temporal variation in

the concentrations of Zn in control *R. cuneata* and in clams exposed to Corpus Christi sediment at 15‰ for 6 weeks. The day-0 animals contained a mean of 85 mg/kg Zn, while at all subsequent sampling times, Zn concentrations in control and exposed animals varied between 68 mg/kg and 78 mg/kg. Exposure, time, and their interaction were not significant.

201. Zinc concentrations in *R. cuneata* showed a slight rising trend during 6 weeks exposure to Ashtabula sediment in fresh water (Figure 132). From a day-0 value of 46 mg/kg, Zn concentrations in exposed animals rose in an irregular fashion to 105 mg/kg at 6 weeks. Concentrations in control animals varied between 76 mg/kg and 82 mg/kg during the same time period. Statistical analysis revealed that time was significant but exposure was marginally insignificant ($P > F = 0.09$).

202. *Palaemonetes pugio*. Time, but not exposure or the interaction of exposure and time, contributed significantly to the patterns of Zn distribution in *P. pugio* during 6 weeks exposure to Corpus Christi sediment at 15‰. In sediment-exposed animals, Zn concentrations dropped from 72 mg/kg at week 1 to 60 mg/kg at week 2 and then rose gradually to 76 mg/kg at week 6. Zinc concentrations in the controls varied irregularly between 63 mg/kg and 73 mg/kg during the same time period.

203. *Palaemonetes kadiakensis*. Exposure, but not time and the interaction of exposure and time, had a marginally significant effect on the accumulation of Zn by *P. kadiakensis* exposed to Ashtabula sediment in fresh water. Day-0 animals contained a mean of 61 mg/kg zinc.

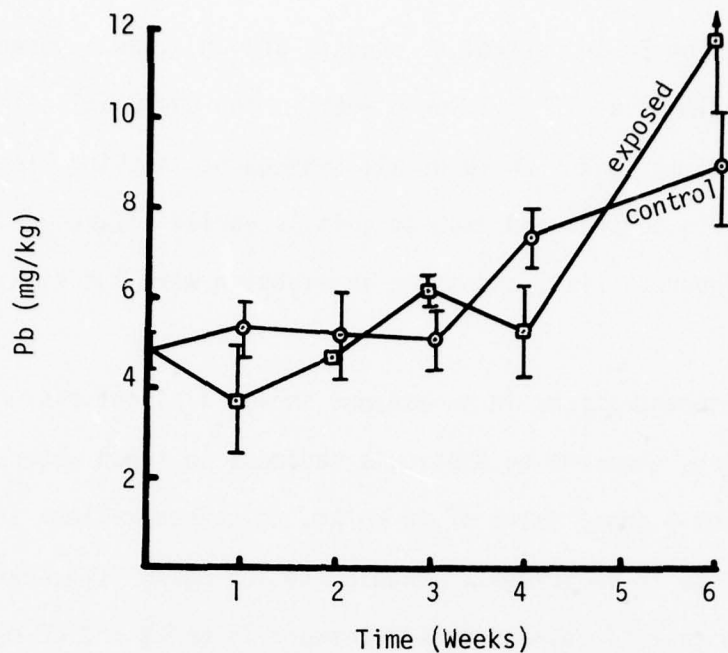


Figure 131. Mean Pb Uptake by *Tubifex* sp.
Exposed to Ashtabula Sediment in fresh water
[Longer Term Studies]

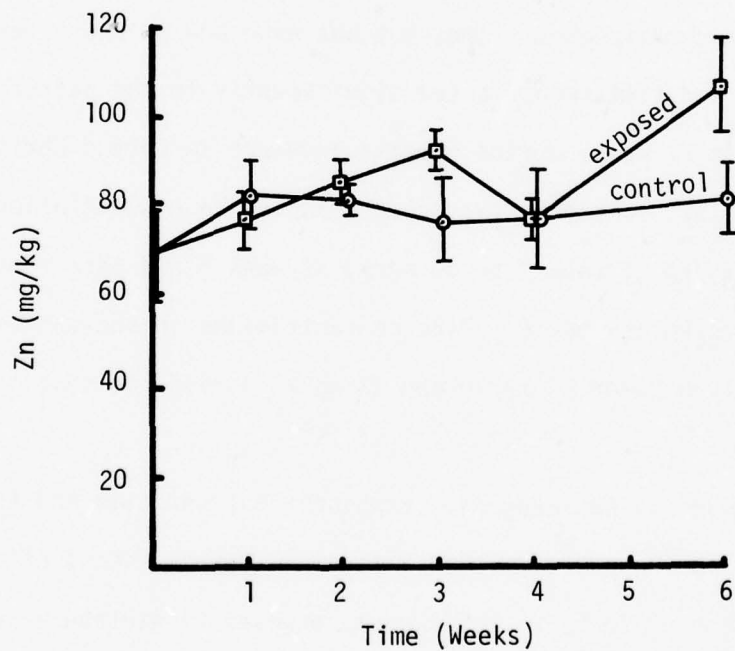


Figure 132. Mean Zn Uptake by *Rangia cuneata*
Exposed to Ashtabula Sediment in fresh water
[Longer Term Studies]

Mean Zn concentrations in exposed shrimp varied between 72 mg/kg and 76 mg/kg during the week 1 to week 4 sampling period, but then dropped to 56 mg/kg at 6 weeks. Zinc concentrations in control animals varied between 55.6 mg/kg and 60 mg/kg during the same time period.

204. *Neanthes arenaceodentata*. Mean Zn concentrations in *N. arenaceodentata* rose from 113 mg/kg at week 1 to 132 mg/kg at week 4 of exposure to Corpus Christi sediment at 30‰. However the day-0 animals contained 123 mg/kg Zn and Zn concentrations in the controls varied between 87 mg/kg and 116 mg/kg during the time course of the experiment. Exposure was found to be marginally insignificant ($P > F = 0.07$), while time and the interaction of exposure and time were highly insignificant.

205. *Tubifex* sp. Exposure was also marginally insignificant ($P > F = 0.06$) in its contribution to the uptake of Zn from Ashtabula sediment in fresh water by *Tubifex* sp. At all but the week 6 sampling time, Zn concentrations were higher in the controls than in the sediment-exposed worms. Zinc concentrations were high in these animals and varied between 174 mg/kg and 276 mg/kg (Figure 133).

Chromium (Cr)

206. Statistical analyses of Cr accumulation by all species during longer term exposures are summarized in Table A18.

207. *Rangia cuneata*. Mean Cr concentrations in control *R. cuneata* and in clams exposed to Corpus Christi sediment at 15‰ for 6 weeks varied irregularly between 3.9 mg/kg and 7.4 mg/kg. The latter value

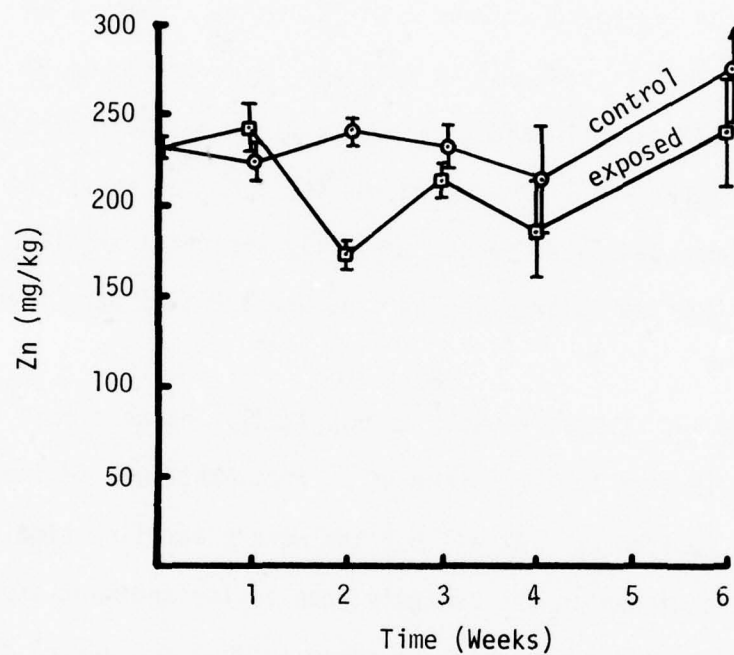


Figure 133. Mean Zn Uptake by *Tubifex* sp.
Exposed to Ashtabula Sediment in fresh water
[Longer Term Studies]

was obtained from 6-week control animals. Exposure, time, and their interaction were not significant.

208. There were slightly greater variations in Cr concentrations in *R. cuneata* exposed to Ashtabula sediment in fresh water and in the corresponding controls (range of means, 5 mg/kg to 13 mg/kg). There was no clear temporal pattern of change, and both main effects and their interaction were insignificant.

209. *Palaemonetes pugio* and *P. kadiakensis* exposed to Corpus Christi and Ashtabula sediments, respectively, had tissue Cr levels below the 1.0 mg/kg detection limit at all sampling times.

210. *Neanthes arenaceodentata* failed to show a significant accumulation of Cr from Corpus Christi sediment at 30‰ during 4 weeks of exposure. Chromium concentrations in exposed animals rose slightly from a day-0 value of 0.7 mg/kg to 1.6 mg/kg at 4 weeks, while Cr concentrations in the controls rose to 1.0 mg/kg in the same time period.

211. *Tubifex* sp. Exposure and the interaction of exposure and time, but not time, contributed significantly to the accumulation of Cr by *Tubifex* sp. during 6 weeks exposure to Ashtabula sediment in fresh water. In exposed animals, Cr concentrations rose from 0.34 mg/kg at day 0 to 0.97 mg/kg in 2 weeks and then dropped to 0.63 mg/kg at 6 weeks (Figure 134). Chromium concentrations in the controls varied from 0.17 mg/kg to 0.65 mg/kg during the same time period.

Mercury (Hg)

212. Statistical analyses of Hg accumulation by all species during the longer term exposures are summarized in Table A19.

213. *Rangia cuneata*. Time, but not exposure or the interaction of exposure and time, contributed significantly to the pattern of Hg distribution measured in the tissues of *R. cuneata* during 6 weeks exposure to Corpus Christi sediment at 15‰S. Mean Hg concentrations in exposed clams rose from a day-0 value of 0.61 mg/kg to 0.82 mg/kg at week 1, dropped to the 0.38 mg/kg to 0.53 mg/kg range at the 3 subsequent sampling times, and finally rose to 0.88 mg/kg at week 6. Mercury concentrations in the controls varied between 0.42 mg/kg and 1.03 mg/kg during the same time period.

214. *R. cuneata* exposed to Ashtabula sediment in fresh water showed a significant accumulation of Hg due to exposure, time, and their interaction. Mean Hg concentrations in the exposed animals rose from a day-0 value of 0.06 mg/kg to 1.29 mg/kg at week 6 (Figure 135). Mean Hg concentrations in the controls varied from 0.13 mg/kg to 0.49 mg/kg during the same time period.

215. *Palaemonetes pugio*. Exposure, time, and their interaction did not contribute significantly to the accumulation of Hg from Corpus Christi sediment at 15‰S by the shrimp *P. pugio*. At all sampling times, Hg concentrations in control animals were equal to or slightly greater than those in the corresponding exposed animals. Mean Hg concentrations in the shrimp tissues were always low and varied between 0.08 mg/kg and 0.20 mg/kg.

216. *Palaemonetes kadiakensis*. Time, but not exposure and the interaction of exposure and time, contributed significantly to the pattern of Hg distribution in the tissues of *P. kadiakensis* during

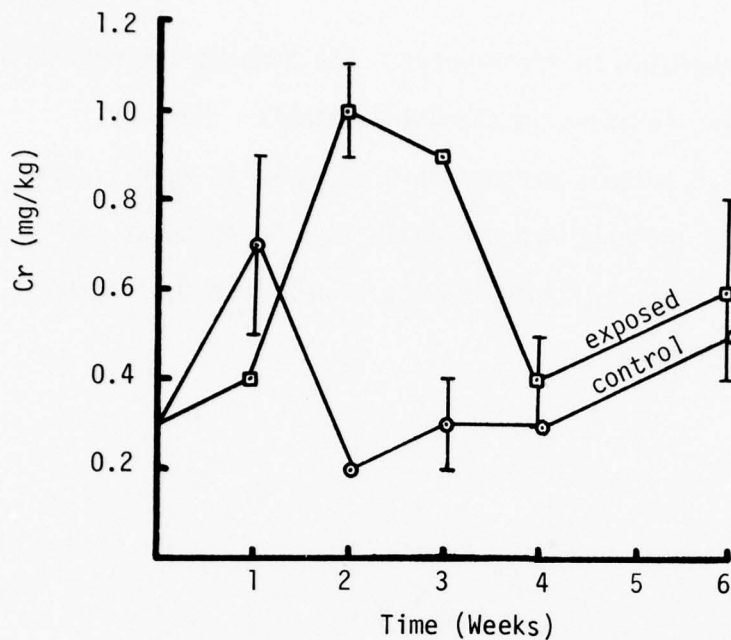


Figure 134. Mean Cr Uptake by *Tubifex* sp.
Exposed to Ashtabula Sediment in fresh water
[Longer Term Studies]

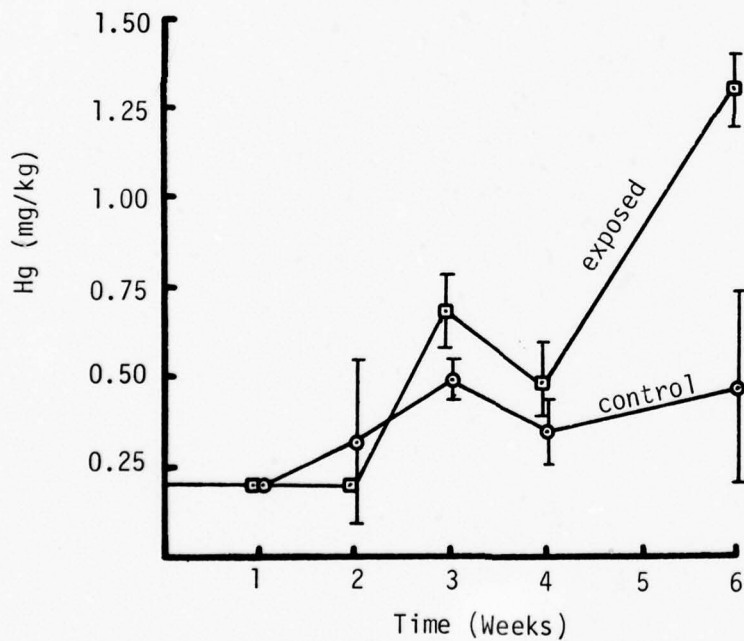


Figure 135. Mean Hg Uptake by *Rangia cuneata*
Exposed to Ashtabula Sediment in fresh water
[Longer Term Studies]

exposure to Ashtabula sediment in fresh water. The highest concentration measured, 0.78 mg/kg, was recorded in the day-0 animals. Mercury concentrations in exposed animals dropped to 0.22 mg/kg at week 1, rose to 0.55 mg/kg at week 3, and then dropped again to 0.38 mg/kg at week 6. Mercury concentrations in control animals rose slowly from 0.17 mg/kg at week 1 to 0.28 mg/kg at week 6.

PART V. DISCUSSION AND CONCLUSIONS

Bioavailability of Sediment-Adsorbed Metals to Benthic Invertebrates

217. Biological laboratory studies were conducted to determine the availability of sediment-adsorbed heavy metals to benthic invertebrates. For these studies, sediments from 3 different locations were selected to provide a range of chemical and physical properties along with elevated heavy metal levels. Five different test organisms (*Rangia cuneata*, *Palaemonetes pugio*, *Palaemonetes kadiakensis*, *Neanthes arenaceodentata*, and *Tubifex sp.*) were exposed to these sediments for periods up to 6 weeks to determine if the sediment-associated metals were available to the test animals.

218. Results obtained from this study on the bioavailability of the sediment-adsorbed heavy metals to the benthic invertebrates are summarized in Table 13 (short-term studies) and Table 14 (longer term studies). A total of 20 experimental exposures involving 3 sediments, 5 benthic invertebrate species, 3 salinities and exposure times up to 6 weeks were conducted. Eight heavy metals were measured in the tissues of all experimental animals, and 2 additional metals were analyzed in animals from selected experiments. Of the resulting 136 metal-organism-sediment combinations, only 49 (36%) demonstrated a statistically significant relationship between exposure to sediment and heavy metal concentrations in the tissues of the experimental animals. In 13 of the 49 cases in which a statistically significant effect of exposure to sediment on heavy metal uptake was demonstrated, the effect of sediment was inverse or negative.

Table 13
Summary of Bioavailability of Sediment-Adsorbed
Heavy Metals to Benthic Invertebrates During Short-Term Exposures

Metal	Texas City Sediment			Corpus Christi Sediment			Ashtabula Sediment		
	<i>Rangia</i>	<i>Palaemonetes</i>	<i>Neanthes</i>	<i>Rangia</i>	<i>Palaemonetes</i>	<i>Neanthes</i>	<i>Rangia</i>	<i>Palaemonetes</i>	<i>Tubifex</i>
Cd	0	-	0	0	0	0+	0	0	0
Cr	0	+	+	0	0	0	0	0	0
Cu	0	0	+	0	-	0+	0	0	0
Fe	0	+	0	0	+	0+	+	+	+
Hg							0	0	0
Mn	+	+	0	-	0	0	0	0	0
Ni	0	-	0	-	-	0	0	-	0
Pb	0	0	+	0	+	+	+	0	+
V							+	+	-
Zn	0	-	0	0	+	0+	0	-	-

Note:

- + = Statistically significant effect of exposure, and/or the interaction of exposure with salinity, time, or both on the concentrations of the heavy metal in the animal's tissues.
- = Statistically significant inverse effect of exposure, and/or the interaction of exposure with salinity, time, or both on the concentrations of the heavy metal in the animal's tissues (control animals had significantly higher metal concentrations than did sediment-exposed animals).
- 0 = Exposure to sediment did not contribute significantly to the concentration of the heavy metal in the animal's tissues.
- 0+ = Replicate experiments with *Neanthes* exposed to Corpus Christi sediment at 30‰S gave opposite results.

Statistical analyses of Hg and V were only performed on tissues of *Rangia* and *Palaemonetes* exposed to Ashtabula sediment in fresh water. Hg analyses for other tests were at or below detection limits with few exceptions and V was only studied for Ashtabula sediments.

Table 14

Summary of Bioavailability of Sediment-Adsorbed Heavy
Metals to Benthic Invertebrates During Long-Term Exposures

Metal	<u>Corpus Christi Sediment</u>			<u>Ashtabula Sediment</u>		
	<u>Rangia</u>	<u>Palaemonetes</u>	<u>Neanthes</u>	<u>Rangia</u>	<u>Palaemonetes</u>	<u>Tubifex</u>
Cd	0	0	0	0	+	0
Cr	0	0	0	0	0	+
Cu	0	-	0	0	+	0
Fe	0	-	0	+	+	+
Hg	0	0	0	+	0	0
Mn	0	0	+	-	+	0
Ni	0	0	0	+	0	+
Pb	0	0	0	0	+	0
Zn	0	0	0	0	+	0

Note:

- + = Statistically significant effect of exposure and/or the interaction of exposure and time on the concentration of the metal in the animal's tissues.
- = Statistically significant inverse effect of exposure and/or the interaction of exposure and time on the concentration of the metal in the animal's tissues. (Control animals had significantly higher metal concentrations than did sediment-exposed animals.)
- 0 = Exposure did not contribute significantly to the concentration of the heavy metal in the animal's tissues.

That is, control animals contained significantly higher metal concentrations than did the sediment-exposed animals. Thus, a significant accumulation of a metal from sediment was demonstrated only 16 times (9.5%). In many cases the demonstrated uptake was quantitatively marginal. The short-term experiment in which *Neanthes* was exposed to Corpus Christi sediment at 30‰ was repeated and yielded contradictory results for 4 of the 8 metals analyzed (Table 13). Furthermore, there were only 3 instances in which significant accumulation of a metal was demonstrated in both the short- and long-term exposure for a particular species-sediment-salinity combination (Fe uptake from Ashtabula sediment in fresh water by *Rangia*, *Palaemonetes* and *Tubifex*). There were 10 metal-species-sediment combinations for which a significant exposure-dependent metal uptake was demonstrated in the long-term but not the short-term exposures and 14 combinations for which significant exposure-dependent metal uptake was demonstrated in the short-term but not the long-term exposures.

219. The only metal for which a significant uptake was demonstrated in 50% or more of the short- and long-term exposures was Fe, among the least toxic of the metals investigated (Waldichuk 1974). A significant accumulation of Pb occurred in 5 of the 9 species-sediment combinations utilized in the short-term exposures, but in only 1 of the 6 combinations used in the long-term study. In most cases, the differences in Pb concentrations in control and exposed animals were small. However, *Neanthes arenaceodentata* exposed to Corpus Christi sediment at 30‰ in the short-term study accumulated relatively high concentrations of Pb (17 mg/kg in the first replicate and 7.6 mg/kg in the second). Due to

the relatively high toxicity of Pb and its persistence in animal tissues, this demonstrated accumulation could be ecologically meaningful in terms of direct toxicity to *N. arenaceodentata* and its predators or as a vector for translocation of Pb from sediments to the aquatic food chain. Chromium was accumulated in 2 species-sediment combinations in the short-term study and in 1 combination in the long-term study. *N. arenaceodentata* exposed to Texas City sediment at 30‰ accumulated this metal from sediments to the highest level (5.8 mg/kg). Since the chemical form of Cr has a profound effect on its toxicity (trivalent Cr is many times more toxic than hexavalent Cr, Oshida et al. 1976), the ecological significance of this uptake is uncertain, since the valence of the accumulated metal is not known. With one exception, the other metals were accumulated only once or twice in the short-term and in the long-term exposures. Only Ni was not accumulated at any species-sediment combination in the short-term exposures. However, it was accumulated to a significant extent twice in the long-term exposures (by *R. cuneata* and *Tubifex* sp. exposed to Ashtabula sediment). Vanadium was analyzed only in organisms exposed to Ashtabula sediment. In both *R. cuneata* and *P. kadiakensis*, a significant accumulation of V was demonstrated. Uptake was particularly marked in the clams (a maximum of 11.8 mg/kg V in exposed animals versus 0.66 mg/kg in controls). Little is known about the toxicity of V to aquatic organisms, so the ecological importance of this uptake is uncertain and deserves further investigation.

220. Mercury and Cd were the two heavy metals tested of greatest concern in aquatic and marine pollution studies. This concern stems

primarily from the high toxicity of these metals, their persistence in biological tissues and because of reported incidents involving human Hg and Cd poisoning due to consumption of contaminated shellfish (Holden 1973; Chadwick 1976; Calabrese et al. 1977). A significant accumulation of Cd was demonstrated only once in the short-term studies (*N. arenaceodentata* in Corpus Christi sediment) and once in the long-term exposure (*P. kadiakensis* in Ashtabula sediment). In the first experiment in which *N. arenaceodentata* was exposed to Corpus Christi sediment, a marked accumulation of Cd from sediment was demonstrated (7.7 mg/kg Cd in exposed animals versus 1.4 mg/kg Cd in controls at 32 days: Figure 58). Uptake of Cd from the sediment was not demonstrated in the second exposure. Accumulation of Cd from Ashtabula sediment by *P. kadiakensis*, although statistically significant, was only marginal (0.35 mg/kg Cd in exposed animals versus 0.25 mg/kg in controls at 20 days), and is not considered to be biologically significant. Thus, bioaccumulation of Cd to levels which are ecologically significant, from the standpoint of toxicity or mobilization into the food chain, was demonstrated only once and was not repeated in subsequent exposures of *N. arenaceodentata* to Corpus Christi sediment. In only one test, the long-term exposure of *R. cuneata* to Ashtabula sediment was a significant accumulation of Hg demonstrated. Following 6 weeks exposure, control and sediment-exposed animals contained 0.49 mg/kg and 1.29 mg/kg Hg, respectively, suggesting that an ecologically significant bioaccumulation of Hg from sediment is possible.

221. The 3 other metals studied, Cu, Mn, and Zn, are all essential micronutrients which, however, are toxic in excessive amounts. Copper is

generally the most toxic of these (Waldichuck 1974). There were 10 species-sediment combinations in which a statistically significant accumulation of 1 or more of these metals was demonstrated. Perhaps because of their essentiality, these metals were present at relatively high concentrations, even in the control animals. In only a few cases were the concentrations of these metals substantially higher in the sediment-exposed animals than in the controls (eg Cu in *N. arenaceodentata* exposed to Corpus Christi sediment at 30‰, where concentrations were 92 mg/kg and 27 mg/kg in exposed and control animals, respectively, and Mn in *R. cuneata* exposed to Texas City sediment at 30‰ where concentrations were 102 mg/kg and 16 mg/kg in exposed and control animals, respectively). Such bioaccumulations, particularly of the more toxic copper, could be ecologically significant.

222. In 13 of the metal-species-sediment combinations investigated, a statistically significant inverse relationship was found between sediment exposure and heavy metal accumulation. That is, metal concentrations were significantly higher in control animals than in the corresponding sediment-exposed experiments at most or all sampling times. One explanation for this observation is that metals in solution in the aqueous phase of the test aquaria were adsorbed onto sediment particles rendering the metals less available to the animals. It is well established that sediments, particularly clays, can significantly reduce aqueous heavy metal ion concentrations due to sediment-solute interactions particularly at alkaline pH's (Farrah and Pickering 1977). When this occurs, the concentration of heavy metals would be lower in the water in aquaria containing

sediment than in the water of those without a sediment substrate. In the long-term studies, control aquaria contained a coarser "clean" sediment with a lower proportion of clay-sized particles than the experimental sediments. Equilibration of metal levels between the aqueous phase and the animal tissues would then lead to the observation of lower heavy metal levels in experimental than in control animals. This interpretation is supported by Jackim et al. (1977) who reported that when soft-shell clams *Mya arenaria* were exposed to 5 $\mu\text{g/l}$ aqueous Cd for 7 days, the animals took up a greater amount of the metal when held without a substrate than when held in sand and mud sediments. However, monitoring of the metal content of the aquaria waters during most of the present studies did not indicate concentration changes significantly different from those expected from precision of the analytical methods.

223. In several experiments, the concentration of a metal in the tissues of both the control and sediment-exposed animals varied in an almost parallel fashion during the timecourse of the experiment. This phenomenon was observed at least once in the clams, shrimp, and worms. Examples include Ni in *R. cuneata* exposed to Texas City sediment at 30‰ (Figure 62), Zn in *P. kadiakensis* exposed to Ashtabula sediment in fresh water (Figure 98), and Cd in *N. arenaceodentata* exposed to Texas City sediment at 30‰ (Figure 57). Careful review of the analytical methodology and tissue processing schedules and procedures revealed that these were not the source of the parallel variations. The answer may lie in endogenous cyclic variations in trace metal turnover rates in the animals. It is well established that there is a direct correlation

between the turnover rate of many heavy metals in animal tissues and the metabolic rate of animal (Fagerstrom 1977). Thus, a decreased metabolic rate would result in a slower exchange of metals between the ambient medium and the tissues causing the metal to accumulate to higher concentrations in the tissues. An increased metabolic rate would result in the opposite trend assuming constant levels of ambient metals. Thus endogenous cyclical variations in the metabolic rate of the animals would be reflected in cyclical changes in the concentrations of metals in their tissues. Each metal would behave differently, depending on its turnover rate in the animal tissues. There are several reports of large scale seasonal cycles of tissue heavy metals in benthic invertebrates (Galtsoff 1964; Bryan 1974; Ireland 1974; Fowler and Oregioni 1975; Frazier 1975, 1976). However, there are relatively few reports of short-term variations in metals levels in animals maintained under constant conditions in the laboratory. Phillips (1977), in a study of the effects of salinity on Zn uptake by the mussel *Mytilus edulis*, reported wide variations in the concentration of Zn in his control animals (maintained in natural seawater without added metal) over the 300-hour course of the experiments. In the experiments reported here, the control animals almost never maintained constant tissue levels of the metals analyzed during the time course of the experiment. Thus, in the situations where the concentration of a metal in both control and sediment-exposed animals varied cyclically in a parallel fashion, the variations may be interpreted to reflect changes in the equilibrium constant for the metal between the tissue and aqueous phases, whereas the difference in actual tissue metal concentration

between the controls and the exposed animals at any sampling time reflects the influence of the sediment

224. There were important inter- and intra-species differences in the bioavailability of sediment-adsorbed heavy metals. Surprisingly the clam *Rangia cuneata* showed a significant accumulation of metals from the sediments fewer times than did either the shrimp or the worms. Bivalve molluscs have been widely recommended as test organisms for monitoring the levels of pollutants, including heavy metals, in the marine environment (Goldberg 1975). Partly for this reason, a large part of the recent research on the accumulation of heavy metals from water, food, and sediments has utilized benthic molluscs.

225. In the present investigation, there was only one case in which all three species accumulated the same metal from the same sediment. In both the short-term and long-term studies, the clam, the shrimp and the worm accumulated Fe from Ashtabula sediment. In all the other experiments in which the uptake of a metal was demonstrated from a particular sediment, only one or two of the species tested accumulated the metal. In most cases the species accumulating a particular metal from one sediment did not accumulate the same metal from the other two sediments. For instance, in the short-term experiments, *R. cuneata* and *P. pugio*, but not *N. arenaceodentata*, accumulated Mn from Texas City sediment but none of the animals accumulated Mn from the other two sediment. *N. arenaceodentata* accumulated Pb from Texas City and Corpus Christi sediment, while *Palaemonetes* accumulated this metal from Corpus Christi but not Texas City or Ashtabula sediment. The ability of a particular species to

accumulate a metal from one sediment but not from another would suggest that the chemical and physical form as well as the concentration of the metal in the sediment determines the bioavailability of that metal to the species in question. On the other hand, the observation that one species is able to accumulate a particular metal from a sediment while another species is not would suggest that the chemical and physical forms of a metal that are available for bioaccumulation are different for different species.

226. These interspecies differences in the ability to bioaccumulate different forms of sediment-adsorbed metals may be related to the pH and Eh of the gut contents, the rate of passage of materials through the gut, and to the chemical and permeability properties of the general integument. A micellar layer of sulfated mucopolysaccharides on the surface of the body wall of some annelids and molluscs may either favor or inhibit metal adsorption through the integument. The chitonized exoskeleton of crustaceans may prevent direct adsorption of heavy metals from the medium, but cuticular quinone-tanned proteins in some species may chelate metals (Horowitz and Presley 1977).

227. Many other biotic factors can affect the rate of uptake of heavy metals as well as which chemical forms of metals are available for accumulation. Nutritional status and biochemical composition (reflected in the condition index), which vary seasonally particularly in molluscs, have a marked effect on the rate of heavy metal accumulation and the equilibrium concentration of metals in the tissues of aquatic animals (Phillips 1977). Since the animals used in the investigation reported

here were collected from the same geographic area but at different times of year over a 2-year period, it is not surprising that 0-day controls contained widely varying tissue metals concentrations and the ability and extent of heavy metal uptake from the sediments varied from one experiment to another.

228. In an effort to determine the effect of salinity on the uptake of heavy metals from sediment, *R. cuneata* and *P. pugio* were exposed to Texas City and Corpus Christi sediment at both 15‰ and 30‰. A total of 32 metal-species-sediment combinations were compared at the two salinities. There were 22 instances in which salinity had a statistically significant effect on the concentration of a heavy metal in the tissues of the animals (Table 15). It should be stressed that, in most cases where salinity did exert a significant effect, sediment exposure was without significant effect on the tissue heavy metal levels measured. Thus, in most cases, the significant effect of salinity reflects a change in the equilibrium distribution of the metal between the tissues and the water in response to a change in the concentration of the medium. There were 12 instances in which animals at the lower salinity had significantly higher tissue heavy metal concentrations than those at the higher salinity. There were 10 instances in which animals at the higher salinity had significantly higher tissue heavy metal concentrations than those at the lower salinity. In all cases where the statistical significance of salinity was demonstrated, 2 metals, Cr and Fe, were present at higher concentrations in animals 15‰ than at 30‰ and 1 metal, Pb, was present at a higher concentration in animals at 30‰ than at 15‰.

Table 15

Summary of the Statistical Analysis of the Effect of Salinity on
the Concentration of Metals in the Tissues of Experimental Animals

<u>Metal</u>	<u>Texas City Sediment</u>		<u>Corpus Christi Sediment</u>	
	<u>Rangia</u>	<u>Palaemonetes</u>	<u>Rangia</u>	<u>Palaemonetes</u>
Cd	+(15)	0	+(30)	0
Cr	+(15)	+(15)	0	+(15)
Cu	+(15)	-	+(15)	+(30)
Fe	+(15)	+(15)	0	0
Mn	+(30)	+(15)	+(30)	0
Ni	0	+(30)	+(15)	+(30)
Pb	+(30)	0	+(30)	+(30)
Zn	+(15)	+(30)	0	+(15)

Note:

+ = Salinity and/or the interaction of salinity with exposure, time, or both contributed significantly to the concentration of metal in the animal's tissues. The number in parentheses is the salinity at which the metal concentration in the animal's tissues was higher.

0 = Salinity and its first-order interactions with exposure and time were not significant.

The results for the other 5 metals, Cd, Cu, Mn, Ni and Zn, were mixed. *R. cuneata* had higher tissue Mn concentrations at 30‰ than at 15‰ during exposure to both sediments, while *P. pugio* had higher tissue Mn concentrations during exposure to Texas City sediment at 15‰. The opposite trend was seen for Ni. *P. pugio* had higher tissue Ni concentrations at 30‰ during exposure to both sediments, while *R. cuneata* had higher tissue Ni concentrations during exposure to Corpus Christi sediment at 15‰. Copper concentrations were higher in *R. cuneata* exposed to both sediment at 15‰, while in *P. pugio*, tissue Cu concentrations were higher in animals exposed to Corpus Christi sediment at 30‰. The salinity effect for the other metals was opposite for the two sediments.

229. Several investigators have reported an inverse relationship between salinity and the rate and extent of heavy metal uptake by marine animals (Hutchinson 1974; Phillips 1976, 1977; Jackim et al. 1977; Wright 1977). A change in the salinity and thus the ionic strength of the medium results in speciation of aqueous and probably also some sediment-adsorbed heavy metals to chemical forms which may have increased or decreased availability for biological accumulation (Zirino and Yamamoto 1974). In most cases the metals are rendered less soluble and less bioavailable by an increase in salinity. However, the behavior of each heavy metal in a changing ionic environment is different, and the presence of a sedimentary particulate phase in the system increased the complexity of the interactions. It is interesting to note that in the long-term studies where comparisons are easier to make, there was only one case in which a significant accumulation of a heavy metal from Corpus

Christi sediment at 15‰ or 30‰ was demonstrated (Table 14). On the other hand a significant accumulation of a heavy metal by animals exposed to Ashtabula sediment in fresh water was demonstrated 12 times. Thus, it would appear that the salinity of the ambient medium does have an important effect on the bioavailability of both aqueous and sediment-adsorbed heavy metals to benthic invertebrates.

230. Depuration tests were performed on all organisms exposed to the Corpus Christi sediment as well as some of those exposed to Texas City and Ashtabula sediments. Since observed metal uptake was limited, the depuration tests gave statistically significant results for only a few of the metals. Typical depuration tests in which metal loss occurred, are those shown in Figures 85 and 113 for Pb and Cr, respectively, in *N. arenaceodentata* exposed to Texas City sediment. For these, the metals were depurated in 8 days to levels not significantly different from those in the control worms. However, in some cases where uptake occurred during exposure to sediment, the metal level remained the same or, in several instances, increased slightly during depuration. For example, Pb in *Tubifex* from the Ashtabula sediment exposure, Figure 88, increased slightly over an 8-day depuration period.

231. Among those cases where there was a significant accumulation of a metal from sediment and depuration was attempted, only 7 cases of metal loss during depuration were shown. Among those in which no loss during depuration was observed, 3 involved Pb.

Heavy Metal Burdens in Natural Populations of Benthic Invertebrates

232. The concentrations of heavy metals in the tissues of fresh water and marine invertebrates show very large seasonal, geographic and inter- and intra-species variations. Some of the causes of this variability have been discussed in the literature review section of this report and include salinity, temperature, nutritional status, size of organism, and in particular ambient levels of heavy metals in different soluble and adsorbed forms. Relatively little data has been published on the "normal" levels of heavy metals in natural populations of the five species of invertebrates used in the present investigation. The published values have been summarized in Table 16. For comparison, the range of concentrations of heavy metals found in the tissues of the three phyletic groups, molluscs, crustaceans, and annelids, used in this investigation are summarized in Table 17. Table 18 summarizes the data for day-0 control concentrations of heavy metals in the experimental animals acclimated to the three test salinities. Inspection of these 3 tables reveals that in most cases, day-0 heavy metal concentrations in the animals fall within the range of published values for the same or similar species. In most cases, heavy metal values for the animals fell in the lower part of the range of published values, indicating that the test organisms were relatively uncontaminated with pollutant heavy metals and that the analytical methodology was good, since an important problem with atomic absorption analysis is spuriously high values due to background and matrix effects.

Table 16
Heavy Metal Concentration Ranges Reported
For Animals Similar to Test Species
mg/kg (dry weight)

Metal	Pelecypod ¹ molluscs	Decapod ² crustaceans	Polychaete ³ worms	<i>Nereis</i> ⁴ <i>diversicolor</i>
Cd	0.07-140	0.05-32	-	0.1
Cr	.08-288	0.08	-	0.5
Cu	2.1-2100	2.1-435	6.8-7.0	18
Fe	6.0-3500	25-30	-	450
Hg	.01-1.9	<0.0001-1.0	0.01-0.35	-
Mn	1.4-70	1.4-1.9	-	9
Ni	0.1-174	1.1-12.3	-	1.5
Pb	0.3-117	0.7-8.3	-	5
Zn	0.3-10460	57-330	-	170

¹Pelecypod molluscs, Reish et al. 1975; 1976; 1977.

²Decapod crustaceans, Reish et al. 1975; 1976; 1977.

³Polychaete worms, Reish et al. 1975; 1976; 1977.

⁴*Nereis diversicolor*, Bryan 1976.

Table 17
Heavy Metal Concentrations Previously Reported for Test Animals

Species	Location	‰S	mg/kg (dry weight)							
			Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
¹ <i>Rangia cuneata</i>	San Antonio Bay, Texas	estuarine	--	--	25	--	--	--	1.1	5.1
² <i>Palaemonetes pugio</i>	Bavon, Virginia	estuarine	--	--	--	--	11.4	--	0.2	--
	Pensacola, Florida	20	0.196	--	--	--	--	--	--	--
³ <i>Neanthes arena-ceodentata</i>	Long Beach, California	32	--	0.5 1.6	--	--	--	--	--	--
⁴ <i>Tubifex tubifex</i>	Illinois, R., Illinois	0	1.1	10	23	--	--	11	17	41

Note:

-- = Not determined or below detection limits.

¹*Rangia cuneata*, Sims and Preseley 1977.

²*Palaemonetes pugio*, Drifmeyer and Odum 1975; Nimmo et al. 1977.

³*Neanthes arenaceodentata*, Oshida et al. 1976.

⁴*Tubifex tubifex*, Mathis and Cummings 1973.

Table 18
The Range of Mean Heavy Metal Concentrations
in Control Animals for this Study

Metal	‰S	mg/kg			
		<i>Rangia</i>	<i>Palaemonetes</i>	<i>Neanthes</i>	<i>Tubifex</i>
Cd	0	1.4-1.7	0.03-0.28	-	0.04-0.4
	15	0.12-1.9	0.07-0.11	-	-
	30	0.48	0.06	0.20-0.42	-
Cr	0	4.2-5	<1-1.6	-	0.3
	15	3.1-4.5	<0.2-0.26	-	-
	30	3.0	<0.20	0.7-3.1	-
Cu	0	12-16	54-91	-	7-9
	15	14-22	47-130	-	-
	30	8.7	93-181	31-61	-
Fe	0	220-279	51	-	440-561
	15	148-295	20-40	-	-
	30	176	20-22	67-119	-
Hg	0	0.06	0.78	-	0.22
	15	<0.24-0.61	0.08	-	-
	30	-	-	-	-
Mn	0	9-20	13-17	-	8-9
	15	4.1-38	9.3-19	-	-
	30	8.6	12-18	10-20	-
Ni	0	14-20	0.8-1.6	-	<1-2
	15	6.6-30	<0.7	-	-
	30	7.2	<1.0	5.5-14.8	-
Pb	0	0.3-2.3	0.11-0.52	-	4-4.8
	15	<0.1-2.7	<0.1-0.16	-	-
	30	1.8	0.3	0.76-1.9	-
Zn	0	46-84	61-84	-	222-234
	15	55-83	71-79	-	-
	30	59	73-76	123-195	-

Metal Forms as Indicators of Availability

233. Based upon the results of this study it has not been possible to relate the bioavailability of a metal with its chemical or physical form within the test sediment. The sediments used in these studies were chosen for their high level of heavy metals, ranging from moderately polluted to highly polluted for a number of the metals under investigation. For this reason, it was expected that substantial bioaccumulation of metals by the test organisms would occur. Such was not the case.

234. As has been previously discussed, the number of occurrences of statistically significant bioaccumulation was small (<30%). Where uptake was demonstrated, it varied not only between species, metals, salinities, and test sediments, but also between tests that differed only in the time of year that they were run. Obviously, attempts to correlate particular forms of metals, as determined by the various chemical extractants to bioavailability when accumulation is limited will not be too successful. Therefore, based upon limited data obtained from 3 test sediments, it is not possible to propose a simple extraction scheme that might indicate bioavailability of sediment-sorbed metals to benthic organisms.

235. It is often assumed that a metal's bioavailability is determined by its presence in the soluble form. However, uptake did not occur for all metals found associated with the interstitial waters of the sediments tested. This lack of accumulation by test organisms may be related not so much to the amount of metal present in the soluble

form as its actual chemical species. For instance, Sundra et al. (1978) have demonstrated that toxicity of Cd to *Palaemonetes pugio* is a function of the amount of free Cd ion, not necessarily the amount of soluble Cd present.

236. One result of this study has been to indicate the uselessness of bulk metal analyses of sediments for predicting the availability and therefore the effects of sediment-sorbed metals on benthic animals. For example, a comparison of the EPA Region V suggested bulk sediment criteria (see Appendix C) with bulk metal analysis of the Ashtabula test sediment indicates that 5 of the metals used in this study exceeded Region V's definition of heavily polluted material, but only 1 of these (Fe) was taken up during the short-term studies. Although all 5 were taken up during the longer term studies, not all were accumulated by each test species.

237. This lack of correlation between bulk metal analysis and bioaccumulation is even more pronounced for the estuarine sediments. A comparison of EPA Region VI bulk metal disposal guidelines (Appendix C) with the Texas City and Corpus Christi sediments indicates a number of metals exceeded the criteria. Although 3 metals in the Texas City sediments exceeded the criteria level, only 1 (Cr) was accumulated by test organisms.

238. Of the 5 metals from Corpus Christi sediments that exceeded the criteria only Pb and Zn were accumulated during the short-term exposures. During longer exposures, none of these 5 were taken up.

PART VI. SUMMARY

239. Laboratory studies were conducted to determine the bioavailability to benthic invertebrates of sediment-adsorbed heavy metals. Five species of benthic invertebrates (clams *Rangia cuneata*, shrimp *Palaemonetes pugio* and *P. kadiakensis*, and worms *Neanthes arenaceodentata* and *Tubifex* sp.) were exposed to natural sediments from 3 sources (Texas City, Corpus Christi, and Ashtabula) for periods up to 6 weeks. The accumulation of 8 heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) by all species and of 2 metals (Hg and V) by selected species were measured. Exposures were performed in 15‰ and 30‰ sea water (Texas City and Corpus Christi sediments) or in fresh water (Ashtabula sediment).

240. Twenty experimental exposures were performed over a 2-year period. Of the resulting 136 metal-species-sediment combinations, only 49 (36%) demonstrated a statistically significant relationship between exposure to sediment and heavy metal concentrations in the tissues of the experimental animals. In 13 of these cases, the effect of the sediment was inverse. That is, control animals contained significantly higher metal concentrations than did the sediment-exposed animals. Thus, a significant accumulation of a metal from sediment was demonstrated only 36 times (26.5%).

241. The marine worm *Neanthes arenaceodentata* was exposed to Corpus Christi sediment at 30‰ in 2 experiments and contradictory results were obtained for 4 of the 8 metals analyzed. There were 10 metal-species-sediment combinations in which a significant exposure dependent metal

uptake was demonstrated in the long-term but not the short-term exposures and 14 combinations for which a significant exposure-dependent metal uptake was demonstrated in the short-term but not the long-term exposures. Only Fe was accumulated by all species exposed to a sediment (Ashtabula) in both the long-term and short-term exposures.

242. In many cases where a statistically significant accumulation of a metal from a sediment was demonstrated, the uptake was quantitatively marginal and of doubtful ecological significance. A demonstrated metal accumulation was considered ecologically significant if the metal had been demonstrated to be toxic to aquatic organisms or to consumers of fishery products and if the concentration of that metal in sediment-exposed animals was several-fold higher than its concentration in control animals. Such an accumulation could be directly toxic to the benthic invertebrates or their predators and could represent a route of mobilization of toxic heavy metals from sediments into the aquatic food chain. Of the heavy metals analyzed, Hg and Cd are considered to be the most toxic. Accumulation of Hg to a concentration that is of potential ecological significance was demonstrated once, in the clam *R. cuneata* exposed to Ashtabula sediment in fresh water for 6 weeks (1.29 mg/kg Hg in exposed animals versus 0.49 mg/kg in controls). Of the 16 Cd species-sediment combinations investigated, only 1 resulted in an ecologically significant accumulation of Cd from sediment. This occurred in the marine worm *N. arenaceodentata* exposed to Corpus Christi sediment at 30‰ for 32 days. Sediment-exposed animals contained 7.7 mg/kg Cd and controls contained 1.4 mg/kg. Other single instances of the

accumulation of ecologically significant amounts of toxic heavy metal from sediment included Pb by *N. arenaceodentata* from Corpus Christi sediment, Cr by *N. arenaceodentata* from Texas City sediment, Cu by *N. arenaceodentata* from Corpus Christi sediment, and V by *R. cuneata* Ashtabula sediment.

243. In 13 of the metal-species-sediment combinations investigated, a statistically significant inverse relationship was found between sediment exposure and heavy metal accumulation. Metal concentrations were significantly higher in control animals than in the corresponding sediment-exposed individuals. This suggests that adsorption of aqueous phase heavy metals onto sediment particulates might render the metals less bioavailable to the benthic invertebrates, although such changes in aqueous metal levels were not demonstrated.

244. Parallel cyclical variations in heavy metal concentrations in control and sediment-exposed animals were observed in several experiments. These variations may be related to changes in the rate of turnover of heavy metals in the animal tissues as a result of the cyclical variations in metabolic rate characteristic of many benthic invertebrate species.

245. There were substantial inter- and intra-species differences in the accumulation of heavy metals from different sediments. The clam *R. cuneata* accumulated heavy metals from sediments fewer times than did worms or shrimp. The ability of a particular species to accumulate a metal from one sediment but not from another suggests that the chemical and physical form as well as the concentration of the metal in the

sediment determines the bioavailability of that metal to the species in question. The observation that one species is able to accumulate a particular metal from a sediment while another species is not suggests that the chemical and physical forms of a metal that are available for bioaccumulation are different for different species.

246. There were 32 metal-species-sediment combinations in which heavy metal accumulation was compared at 2 salinities, 15‰ and 30‰. There were 22 instances in which salinity had a statistically significant effect on the concentration of a heavy metal in the tissues of exposed and control animals. In 12 instances, animals at the lower salinity had significantly higher body burdens of a metal and in 10 instances those at the higher salinity contained higher concentrations of the metal. This undoubtedly reflects in part the effects of salinity on metal speciation in the aqueous and sediment phases of the system and on the adsorption-desorption kinetics of sediment-adsorbed heavy metals. Each metal behaves differently.

247. Eight-day depuration tests following 8 days exposure to sediment gave variable results. In a few cases in which a significant accumulation of a metal during exposure was demonstrated, the animals released the heavy metal to control levels in 8 days. In other instances, tissue heavy metal concentration remained unchanged or even rose during the depuration period.

248. Heavy metal concentrations in the 0-day control animals used in these investigations were generally in the lower part of the range of published values for natural populations of the same or similar species.

249. The results of this investigation indicate that it is extremely difficult to precisely assess the bioavailability of sediment-adsorbed heavy metals to benthic invertebrates. The relative availability of different heavy metals varies substantially and is influenced by the animal species used and the salinity at which exposure is performed. Replicate exposures performed under identical conditions yielded contradictory results, indicating the possibility of seasonal variations in the ability of animals to accumulate heavy metals from sediment. In the evaluation of the bioavailability of heavy metals from dredged material, 2 or more species of different phyletic position (e.g., molluscs, annelid worms, shrimp) should be used and the exposures should be conducted at a salinity similar to that at the disposal site. Exposures of 3 to 4 weeks seem adequate. Longer exposures did not result in a substantial increase in heavy metal accumulation.

250. The bioaccumulation of metals by test organisms in this study could not be correlated to any particular metal forms extracted from the test sediments and a simple extraction method for predicting bioavailability of sediment-sorbed metals to benthic invertebrates was not developed. However, results indicated that bulk analysis of metals in sediments was useless in predicting availability and environmental effects of the sediment-associated metals on benthic organisms. For this reason, it is recommended that bioassays be performed on sediments containing high levels of metals to determine these effects prior to open water disposal.

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Appendix A

Tables A1-A19. Analysis of variance of heavy metal uptake by five species of benthic invertebrates exposed to three sediments in short-term and long-term tests. For all tables, Source = source of variation; df = degrees of freedom; M.S. = mean square; F = ratio of treatment mean square to error mean square; $P > F$ = probability of a larger F value.

Table A1
Analysis of Iron Uptake
by Species Exposed to Various Sediments
Short-Term Studies

<u>Sediment</u>	<u>Source</u>	<u>df</u>	<u>Sum of Squares</u>	<u>M.S.</u>	<u>F</u>	<u>P>F</u>
Texas City			<i>Rangia cuneata</i>			
	Model	18	126459.0	7025.500	3.18	0.002
	Exp	1	9904.5	9904.500	3.58	0.07
	Sal	1	20943.2	20943.200	7.57	0.01
	Time	5	34015.2	6803.040	2.46	0.05
	Exp*Sal	1	1840.1	1840.100	0.67	0.42
	Exp*Time	5	25802.7	5160.540	1.86	0.13
	Sal*Time	5	33953.3	6790.660	2.45	0.06
	Error	31	85779.8			
	Total	49	212238.8	2767.090		
Corpus Christi	Model	11	5056.8	459.709	2.97	0.28
	Exp	1	90.8	90.800	0.65	0.50
	Sal	1	1728.0	1728.000	12.43	0.07
	Time	3	927.0	309.000	2.22	0.33
	Exp*Sal	1	675.0	675.000	4.86	0.16
	Exp*Time	3	770.8	256.933	1.85	0.57
	Sal*Time	2	866.0	433.000	3.12	0.24
	Error	2	278.0	139.000		
	Total	13	5334.8			

(Continued)

Table A1 (Fe, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula			<i>Rangia cuneata</i>			
	Model	9	6762632.2	751514.680	4.50	0.01
	Exp	1	1763333.3	1763333.300	8.85	0.01
	Time	4	2657602.7	664400.670	3.34	0.05
	Exp*Time	4	2342696.2	585674.050	2.94	0.07
	Error	12	2390591.7	199215.972		
	Total	21	9154223.9			
Ashtabula			<i>Palaemonetes kadiakensis</i>			
	Model	9	306021.1	34002.344	11.32	0.02
	Exp	1	144050.3	144050.300	46.14	0.003
	Time	4	67308.1	16827.025	5.39	0.07
	Exp*Time	4	94662.7	23665.675	7.58	0.04
	Error	4	12487.5	3121.875		
	Total	13	318508.6			
Texas City			<i>Palaemonetes pugio</i>			
	Model	16	95193.4	5949.588	10.52	0.0001
	Exp	1	23904.3	23904.300	25.69	0.0001
	Sal	1	6414.2	6414.200	6.89	0.014
	Time	3	17257.4	5752.467	6.18	0.002
	Exp*Sal	1	9939.8	9939.800	10.68	0.003
	Exp*Time	5	28583.1	5716.620	6.14	0.0005
	Sal*Time	3	9094.6	3031.533	3.26	0.036
	Error	29	26984.0	930.500		
	Total	45	122177.4			

(Continued)

Table A1 (Fe, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
<i>Palaeomonetes pugio</i>						
Corpus Christi (Second Run)	Model	11	11047.2	1004.291	4.73	0.19
	Exp	1	3924.1	3924.100	17.24	0.05
	Sal	1	884.1	884.100	3.88	0.19
	Time	3	2129.5	709.833	3.12	0.25
	Exp*Sal	1	1704.1	1704.100	7.49	0.11
	Exp*Time	3	1175.2	391.733	1.72	0.39
	Sal*Time	2	1230.2	615.100	2.70	0.27
	Error Total	2 13	455.2 11502.4	227.600		
<i>Neanthes arenaceodentata</i>						
Texas City	Model	5	12967.5	2593.500	0.93	0.54
	Exp	1	3132.9	3132.900	1.13	0.35
	Time	4	9834.6	2458.650	0.89	0.55
	Error Total	4 9	11098.6 24066.1	2774.700		
Corpus Christi (First Run)	Model	10	552775.8	55277.580	24.41	0.0001
	Exp	1	105347.1	105347.100	50.93	0.0001
	Time	5	350759.1	70151.820	33.91	0.0001
	Exp*Time	8	96669.6	24167.400	11.68	0.002
	Error Total	8 18	16549.0 569324.8	2068.600		
Corpus Christi	Model	4	744.0	186.000	0.20	0.92
	Exp	1	50.0	50.000	0.05	0.83
	Time	3	694.0	231.333	0.25	0.86

(Continued)

Table A1 (Fe, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P F
Corpus Christi (Second Run)	Error	3	2828.0	942.700		
	Total	7	3572.0			
Ashtabula			<i>Neanthes arenaceodentata</i>			
			<i>Tubificex sp.</i>			
	Model	11	2380300.9	216390.990	7.62	0.002
	Exp	1	586092.9	586092.900	19.34	0.001
	Time	5	985463.2	197092.640	6.50	0.01
	Exp*Time	5	808744.8	161748.960	5.34	0.01
	Error	10	303052.5	30305.250		
	Total	21	2683353.4			

Table A2
Analysis of Manganese Uptake
by Species Exposed to Various Sediments
Short-Term Studies

<u>Sediment</u>	<u>Source</u>	<u>df</u>	<u>Sum of Squares</u>	<u>M.S.</u>	<u>F</u>	<u>P>F</u>
Texas City	<i>Rangia cuneata</i>					
	Model	18	16486.5	915.917	4.06	0.0003
	Exp	1	2557.9	2557.900	11.35	0.002
	Sal	1	5169.7	5169.700	22.02	0.0001
	Time	5	2184.0	436.800	1.94	0.12
	Exp*Sal	1	521.0	521.000	2.31	0.14
	Exp*Time	5	3938.3	787.660	3.49	0.01
	Sal*Time	5	2115.6	423.120	1.88	0.13
	Error	31	6990.8	225.510		
	Total	49	23477.3			
Corpus Christi	Model	11	547.3	49.755	5.75	0.16
	Exp	1	268.4	268.400	28.76	0.03
	Sal	1	188.0	188.000	20.15	0.05
	Time	3	11.8	3.933	0.42	0.76
	Exp*Sal	1	28.5	28.500	3.06	0.22
	Exp*Time	3	5.3	1.789	0.19	0.90
	Sal*Time	2	45.3	22.650	2.43	0.29
	Error	2	18.7	9.331		
	Total	13	566.0			

(Continued)

Table A2 (Mn, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula	Model	10	<i>Rangia cuneata</i> 2239.1	223.910	2.11	0.11
	Exp	1	277.4	277.400	3.13	0.10
	Time	5	1092.8	218.560	2.46	0.09
	Exp*Time	4	868.9	217.225	2.45	0.10
	Error Total		1065.0 3304.1	88.750		
Ashtabula	Model	4	<i>Palaemonetes kadiakensis</i> 104.5	26.125	1.53	0.38
	Exp	1	28.1	28.100	1.64	0.29
	Time	3	76.4	25.467	1.49	0.38
	Error	3	51.4	17.125		
	Total	7	155.9			
Texas City	Model	14	<i>Palaemonetes pugio</i> 13051.5	932.251	3.21	0.18
	Exp	1	906.0	906.000	2.69	0.20
	Sal	1	4160.2	4160.200	12.35	0.04
	Time	4	112.6	28.150	0.08	0.98
	Exp*Sal	1	4160.2	4160.200	12.35	0.04
	Exp*Time	4	1291.6	322.900	0.96	0.54
	Sal*Time	3	2420.8	806.933	2.40	0.25
	Error	3	1010.8	336.900		
	Total	17	14062.3			
Corpus Christi	Model	11	1561.3	141.936	8.39	0.26
	Exp	1	92.0	92.000	4.36	0.28
	Sal	1	369.0	369.000	17.47	0.15

(Continued)

Table A2 (Mn, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Corpus Christi	Time	3	124.5	41.500	1.96	0.47
	Exp*Sal	1	0.1	0.100	0.01	0.95
	Exp*Time	3	678.2	226.067	10.70	0.22
	Sal*Time	2	297.5	148.750	7.04	0.26
	Error Total	12	21.1 1582.4	21.100		
<i>Palaeomonetes pugio</i>						
Texas City	Model	5	476.0	95.200	2.43	0.20
	Exp	1	3.6	3.600	0.09	0.78
	Time	4	472.4	118.100	3.02	0.15
	Error	4	156.4	39.100		
	Total	9	632.4			
<i>Neanthes arenaceodentata</i>						
Corpus Christi (First Run)	Model	10	10125.3	1012.530	2.39	0.11
	Exp	1	1895.5	1895.500	4.64	0.06
	Time	5	6189.9	1237.890	3.03	0.08
	Exp*Time	4	2039.9	509.975	1.25	0.37
	Error Total	8	3271.5 13396.8	408.940		
Corpus Christi (Second Run)	Model	4	57.1	14.300	4.47	0.12
	Exp	1	2.5	2.500	0.79	0.44
	Time	3	54.6	18.200	5.69	0.09
	Error Total	3	9.6 66.7	3.200		

(Continued)

Table A2 (Mn, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula			<i>Tubificex sp.</i>			
	Model	5	11042.6	2208.520	0.77	0.62
	Exp	1	1537.6	1537.600	0.53	0.51
	Time	4	9505.0	2376.250	0.82	0.57
	Error	4	11527.4	2881.850		
	Total	9	22570.0			

Table A3

Analysis of Copper Uptake
by Species Exposed to Various Sediments
Short-Term Studies

<u>Sediment</u>	<u>Source</u>	<u>df</u>	<u>Sum of Squares</u>	<u>M.S.</u>	<u>F</u>	<u>P>F</u>
Texas City	Model	15	775.9	51.727	1.79	0.30
	Exp	1	0.8	0.800	0.03	0.88
	Sal	1	480.2	480.200	16.66	0.02
	Time	4	181.7	45.425	1.58	0.34
	Exp*Sal	1	0.2	0.200	0.01	0.94
	Exp*Time	4	89.7	22.425	0.78	0.59
	Sal*Time	4	23.3	5.825	0.20	0.22
Corpus Christi	Error	4	115.3	28.825		
	Total	19	891.2			
	Model	9	217.2	24.133	106.83	0.01
	Exp	1	1.9	1.900	8.50	0.10
	Sal	1	206.7	206.700	915.14	0.0004
	Time	2	1.4	0.700	3.06	0.25
	Exp*Sal	1	2.3	2.300	9.98	0.09
	Exp*Time	2	1.1	0.550	2.40	0.29
	Sal*Time	2	3.8	1.900	8.45	0.11
	Error	2	0.5	0.226		
Ashtabula	Total	11	217.7			
	Model	10	1657.6	165.760	1.99	0.13
	Exp	1	112.5	112.500	1.81	0.20

(Continued)

Table A3 (Cu, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula	<i>Rangia cuneata</i>					
	Time	5	922.4	184.480	2.97	0.06
	Exp*Time	4	622.7	155.675	2.67	0.08
	Error	12	744.5	62.042		
	Total	22	2402.1			
	<i>Palaemonetes kadiakensis</i>					
	Model	4	4164.5	1041.125	3.72	0.15
	Exp	1	1035.1	1035.100	3.70	0.15
	Time	3	3129.4	1043.133	3.72	0.15
	Error	3	840.4	280.125		
	<i>Palaemonetes pugio</i>					
	Model	14	6536.8	466.914	2.13	0.29
	Exp	1	1914.1	1914.100	6.25	0.09
	Sal	1	1958.1	1958.100	6.40	0.09
	Time	4	1785.6	446.400	1.46	0.39
	<i>Palaemonetes pugio</i>					
	Exp*Sal	1	39.1	39.100	0.13	0.74
	Exp*Time	4	683.8	170.950	0.56	0.71
	Sal*Time	3	155.2	51.733	0.17	0.91
	Error	3	918.2	306.100		
Corpus Christi	Total	17	7455.0			
	Model	11	22633.7	2057.609	19.98	0.05
	Exp	1	4680.8	4680.800	54.59	0.02
	Sal	1	8374.1	8374.100	97.66	0.01
	Time	3	3307.0	1102.333	12.86	0.07

(Continued)

Table A3 (Cu, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
<i>Palaemonetes pugio</i>						
Texas City	Exp*Sal	1	330.8	330.800	3.86	0.19
	Exp*Time	3	3025.8	1008.600	11.76	0.08
	Sal*Time	2	2915.2	1457.600	17.00	0.06
	Error	2	171.5	85.800		
	Total	13	22805.2			
	<i>Neanthes arenaceodentata</i>					
	Model	5	1772.0	354.400	5.77	0.06
	Exp	1	518.4	518.400	8.44	0.04
	Time	4	1253.6	313.400	5.10	0.07
	Error	4	245.6	61.400		
Corpus Christi (First Run)	Total	9	2017.6			
	Model	10	10648.7	1064.870	5.04	0.01
	Exp	1	2881.5	2881.500	11.46	0.008
	Time	5	4627.7	925.540	4.65	0.02
	Exp*Time	4	3139.5	784.875	3.94	0.04
	Error	9	1792.0	199.100		
Corpus Christi (Second Run)	Total	19	12440.7			
	Model	4	141.5	35.400	0.37	0.82
	Exp	1	4.5	4.500	0.05	0.84
	Time	3	137.0	45.667	0.48	0.72
	Error	3	286.5	95.500		
	Total	7	428.0			

(Continued)

Table A3 (Cu, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula	Model	5	37.9	7.580	2.86	0.17
	Exp	1	0.9	0.900	0.34	0.59
	Time	4	37.0	9.250	3.49	0.13
	Error	4	10.6	2.650		
	Total	9	48.5			

Tubifex sp.

Table A4
Analysis of Cadmium Uptake
by Species Exposed to Various Sediments
Short-Term Studies

<u>Sediment</u>	<u>Source</u>	<u>df</u>	<u>Sum of Squares</u>	<u>M.S.</u>	<u>F</u>	<u>P>F</u>
Texas City			<i>Rangia cuneata</i>			
	Model	15	81.5	5.433	20.80	0.002
	Exp	1	0.3	0.300	1.29	0.32
	Sal	1	73.7	73.700	281.67	0.001
	Time	4	3.7	0.925	3.57	0.12
	Exp*Sal	1	0.1	0.100	0.49	0.52
	Exp*Time	4	0.9	0.225	0.90	0.54
	Sal*Time	4	2.8	0.700	2.67	0.18
	Error	4	1.1	0.262		
	Total	19	82.6			
Corpus Christi	Model	9	0.16	0.018	8.73	0.11
	Exp	1	0.06	0.060	4.32	0.17
	Sal	1	0.08	0.080	53.40	0.02
	Time	2	0.02	0.010	7.83	0.11
	Exp*Sal	1	0.00	0.000	0.01	0.95
	Exp*Time	2	0.00	0.000	1.62	0.38
	Sal*Time	2	0.00	0.000	0.96	0.51
	Error	2	0.0	0.001		
	Total	11	0.2			

(Continued)

Table A4 (Cd, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula			<i>Rangia cuneata</i>			
	Model	3	0.13	0.043	0.84	0.54
	Exp	1	0.01	0.010	0.05	0.83
	Time	3	0.02	0.067	0.17	0.70
	Exp*Time	3	0.10	0.035	0.68	0.46
	Error	4	0.60			
Ashtabula	Total	7	0.73	0.148		
			<i>Palaemonetes kadiakensis</i>			
	Model	4	0.03	0.008	1.38	0.41
	Exp	1	0.00	0.003	0.52	0.52
	Time	3	0.03	0.010	1.67	0.34
	Error	3	0.02			
Texas City	Total	7	0.05	0.007		
			<i>Palaemonetes pugio</i>			
	Model	14	0.46	0.033	4.82	0.11
	Exp	1	0.19	0.190	26.96	0.01
	Sal	1	0.01	0.010	2.02	0.25
	Time	4	0.12	0.030	4.38	0.13
	Exp*Sal	1	0.00	0.004	0.69	0.47
	Exp*Time	4	0.12	0.030	4.14	0.14
	Sal*Time	3	0.02	0.007	1.15	0.45
	Error	3	0.02			
	Total	17	0.48	0.007		

(Continued)

Table A4 (Cd, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Corpus Christi	Model	11	0.04	0.004	1.99	0.38
	Exp	1	0.00	0.001	0.60	0.52
	Sal	1	0.01	0.006	2.61	0.25
	Time	3	0.01	0.002	1.21	0.48
	Exp*Sal	1	0.00	0.002	0.76	0.48
	Exp*Time	3	0.02	0.007	3.43	0.23
	Sal*Time	2	0.00	0.000	0.03	0.97
	Error	2	0.00			
	Total	13	0.04	0.002		
<i>Palaeomonetes pugio</i>						
Texas City	Model	5	0.30	0.060	5.04	0.07
	Exp	1	0.01	0.010	0.97	0.38
	Time	4	0.29	0.072	6.06	0.05
	Error	4	0.04	0.010		
	Total	9	0.34			
	Model	10	105.6	10.560	3.11	0.05
	Exp	1	23.4	23.400	7.81	0.02
	Time	5	60.6	12.120	4.04	0.03
	Exp*Time	4	21.6	5.400	1.80	0.21
Corpus Christi (First Run)	Error	9	27.0	3.000		
	Total	19	132.6			
	Model	4	0.06	0.015	3.27	0.18
	Exp	1	0.03	0.030	6.04	0.09
	Time	3	0.03	0.010	2.34	0.25
	Model	10	105.6	10.560	3.11	0.05
	Exp	1	23.4	23.400	7.81	0.02
	Time	5	60.6	12.120	4.04	0.03
	Exp*Time	4	21.6	5.400	1.80	0.21
Corpus Christi (Second Run)	Error	9	27.0	3.000		
	Total	19	132.6			
	Model	4	0.06	0.015	3.27	0.18
	Exp	1	0.03	0.030	6.04	0.09
	Time	3	0.03	0.010	2.34	0.25
	Model	10	105.6	10.560	3.11	0.05
	Exp	1	23.4	23.400	7.81	0.02
	Time	5	60.6	12.120	4.04	0.03
	Exp*Time	4	21.6	5.400	1.80	0.21
<i>Neanthes arenaceodentata</i>						
Corpus Christi (First Run)	Model	5	0.30	0.060	5.04	0.07
	Exp	1	0.01	0.010	0.97	0.38
	Time	4	0.29	0.072	6.06	0.05
	Error	4	0.04	0.010		
	Total	9	0.34			
	Model	10	105.6	10.560	3.11	0.05
	Exp	1	23.4	23.400	7.81	0.02
	Time	5	60.6	12.120	4.04	0.03
	Exp*Time	4	21.6	5.400	1.80	0.21
Corpus Christi (Second Run)	Error	9	27.0	3.000		
	Total	19	132.6			
	Model	4	0.06	0.015	3.27	0.18
	Exp	1	0.03	0.030	6.04	0.09
	Time	3	0.03	0.010	2.34	0.25
	Model	10	105.6	10.560	3.11	0.05
	Exp	1	23.4	23.400	7.81	0.02
	Time	5	60.6	12.120	4.04	0.03
	Exp*Time	4	21.6	5.400	1.80	0.21

(Continued)

Table A4 (Cd, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Corpus Christi (Second Run)			<i>Neanthes arenaceodentata</i>			
	Error	3	0.01	0.004		
	Total	7	0.07			
Ashtabula			<i>Tubifex</i> sp.			
	Model	5	0.00	0.003	2.58	0.19
	Exp	1	0.00	0.000	0.63	0.47
	Time	4	0.00	0.000	3.06	0.15
	Error	4	0.00	0.001		
	Total	9	0.00			

Table A5
Analysis of Nickel Uptake
by Species Exposed to Various Sediments
Short-Term Studies

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Texas City	Model	15	371.2	24.746	2.67	0.18
	Exp	1	3.9	3.900	0.42	0.55
	Sal	1	41.5	41.500	4.47	0.10
	Time	4	82.0	40.500	2.21	0.23
	Exp*Sal	1	0.4	0.400	0.04	0.85
	Exp*Time	4	118.6	29.650	3.20	0.14
	Sal*Time	4	124.8	31.200	3.36	0.13
	Error	4	37.1	9.277		
	Total	19	408.3			
			<i>Rangia cuneata</i>			
Corpus Christi	Model	11	45.5	4.136	160.10	0.10
	Exp	1	0.0	0.040	0.99	0.43
	Sal	1	2.1	2.100	43.86	0.02
	Time	3	23.6	7.867	165.71	0.01
	Exp*Sal	1	10.8	10.800	228.00	0.003
	Exp*Time	3	6.0	1.990	41.96	0.02
	Sal*Time	2	3.0	1.480	31.18	0.03
	Error	2	0.1	0.048		
	Total	13	45.6			

(Continued)

Table A5 (Ni, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula			<i>Rangia cuneata</i>			
	Model	4	85.5	21.375	1.44	0.40
	Exp	1	12.5	12.500	0.84	0.43
	Time	3	73.0	24.333	1.64	0.35
	Error	3	44.5	14.833		
	Total	7	130.0			
Ashtabula			<i>Palaemonetes kadiakensis</i>			
	Model	4	10.6	2.641	4.12	0.14
	Exp	1	7.4	7.400	11.56	0.04
	Time	3	3.2	1.067	1.64	0.35
	Error	3	1.9	0.641		
	Total	7	12.5			
Texas City			<i>Palaemonetes pugio</i>			
	Model	14	20.9	1.493	6.48	0.07
	Exp	1	4.5	4.500	21.86	0.01
	Sal	1	5.8	5.800	27.76	0.01
	Time	4	3.8	0.950	4.56	0.12
	Exp*Sal	1	1.1	1.100	5.31	0.10
	Exp*Time	4	3.5	0.875	4.19	0.13
	Sal*Time	3	2.2	0.733	3.59	0.16
	Error	3	0.6	0.200		
	Total	17	21.5			

(Continued)

Table A5 (Ni, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Corpus Christi	<i>Palaemonetes pugio</i>					
	Model	11	25.9	2.355	26.94	0.04
	Exp	1	5.2	5.200	46.92	0.02
	Sal	1	7.7	7.700	69.29	0.01
	Time	3	3.7	1.233	11.04	0.08
	Exp*Sal	1	2.3	2.300	20.33	0.05
	Exp*Time	3	5.1	1.700	15.24	0.06
	Sal*Time	2	1.9	0.950	8.55	0.10
	Error	2	0.2	0.100		
	Total	13	26.1			
Texas City	<i>Neanthes arenaceodentata</i>					
	Model	5	7.1	1.414	0.27	0.91
	Exp	1	1.4	1.400	0.26	0.64
	Time	4	5.7	1.425	0.27	0.88
	Error	4	21.1	5.3		
	Total	9	28.2			
	Model	5	16.1	3.216	0.53	0.75
	Exp	1	9.0	9.020	1.49	0.29
	Time	4	7.1	1.775	0.29	0.87
	Error	4	24.3	6.100		
Corpus Christi (First Run)	Total	9	40.4			
	Model	4	19.6	4.895	1.78	0.33
	Exp	1	0.1	0.100	0.04	0.86
	Time	3	19.5	6.500	2.37	0.25
	Error	3	8.2	2.733		
	Total	7	27.8			
	(Continued)					

Table A5 (Ni, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula			<i>Tubifex</i> sp.			
	Model	5	1.1	0.208	1.26	0.42
	Exp	1	1.0	0.960	5.79	0.07
	Time	4	0.1	0.020	0.13	0.97
	Error	4	0.7	0.166		
	Total	9	1.7			

Table A6
Analysis of Lead Uptake
by Species Exposed to Various Sediments
Short-Term Studies

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Texas City			<i>Rangia cuneata</i>			
	Model	15	6.8	0.456	4.34	0.08
	Exp	1	0.3	0.300	3.22	0.15
	Sal	1	4.4	4.400	42.08	0.003
	Time	4	0.5	0.125	1.22	0.43
	Exp*Sal	1	0.1	0.100	0.48	0.53
	Exp*Time	4	0.4	0.100	1.00	0.50
	Sal*Time	4	1.1	0.275	2.62	0.19
	Error	4	0.4	0.105		
	Total	19	7.2			
Corpus Christi	Model	11	3.8	0.346	7.82	0.12
	Exp	1	0.4	0.380	6.28	0.13
	Sal	1	1.8	1.830	29.90	0.03
	Time	3	0.0	0.001	0.02	1.00
	Exp*Sal	1	0.2	0.200	3.02	0.22
	Exp*Time	3	0.1	0.043	0.72	0.63
	Sal*Time	2	1.3	0.630	10.33	0.09
	Error	2	0.1	0.061		
	Total	13	3.9			

(Continued)

Table A6 (PD, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula			<i>Rangia cuneata</i>			
	Model	10	14.7	1.470	4.26	0.01
	Exp	1	1.1	1.100	3.91	0.07
	Time	5	8.8	1.760	6.19	0.005
	Exp*Time	4	4.8	1.200	4.24	0.02
	Error	12	3.4	0.283		
	Total	22	18.1			
Ashtabula			<i>Palaeomonetes kadiakensis</i>			
	Model	4	6.7	1.675	1.28	0.44
	Exp	1	3.1	3.100	2.37	0.22
	Time	3	3.6	1.200	0.91	0.53
	Error	3	3.9	1.302		
	Total	7	10.6			
Texas City			<i>Palaeomonetes pugio</i>			
	Model	14	14.6	1.041	1.14	0.52
	Exp	1	2.6	2.560	2.23	0.23
	Sal	1	2.9	2.890	2.52	0.21
	Time	4	0.1	0.020	0.02	1.00
	Exp*Sal	1	2.0	1.960	1.71	0.28
	Exp*Time	4	3.4	0.850	0.74	0.62
	Sal*Time	3	3.7	1.227	1.07	0.48
	Error	3	3.4	1.133		
	Total	17	18.0			

(Continued)

Table A6 (Pb, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Corpus Christi	<i>Palaemonetes pugio</i>					
	Model	11	12.5	1.136	8.74	0.11
	Exp	1	3.9	3.900	28.67	0.03
	Sal	1	4.4	4.400	32.25	0.03
	Time	3	0.0	0.000	0.06	0.98
	Exp*Sal	1	3.3	3.300	23.99	0.04
	Exp*Time	3	0.4	0.133	0.98	0.54
	Sal*Time	2	0.5	0.250	1.67	0.37
	Error	2	0.3			
	Total	13	12.8	0.150		
Texas City	<i>Neanthes arenaceodentata</i>					
	Model	5	1.2	0.240	2.66	0.18
	Exp	1	0.7	0.730	8.19	0.05
	Time	4	0.5	0.115	1.28	0.41
	Error	4	0.4			
	Total	9	1.6	0.090		
	Model	10	514.5	51.452	11.60	0.001
	Exp	1	142.2	142.180	32.99	0.0004
	Time	5	188.2	37.638	8.73	0.004
	Exp*Time	4	184.2	46.038	10.68	0.003
Corpus Christi (First Run)	Error	8	34.5			
	Total	18	549.0	4.312		
	Model	9	87.2	9.693	10.69	0.001
	Exp	1	22.2	22.250	22.61	0.001
	Time	4	30.6	7.642	7.77	0.007
	Exp*Time	4	34.4	8.605	8.74	0.005
	(Continued)					

Table A6 (Pb, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>A
Corpus Christi (Second Run)			<i>Neanthes arenaceodentata</i>			
	Error	8	7.9	0.986		
	Total	17	95.1			
Ashtabula			<i>Tubifex</i> sp.			
	Model	5	11.7	2.332	5.41	0.06
	Exp	1	8.3	8.280	19.21	0.01
	Time	4	3.4	0.845	1.96	0.26
	Error	4	1.7	0.431		
	Total	9	13.4			

Table A7
Analysis of Zinc Uptake
by Species Exposed to Various Sediments
Short-Term Studies

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Texas City	Model	15	2456.1	163.740	4.50	0.08
	Exp	1	5.0	5.000	0.14	0.73
	Sal	1	2163.2	2163.200	59.39	0.002
	Time	4	134.3	33.575	0.92	0.53
	Exp*Sal	1	1.8	1.800	0.05	0.84
	Exp*Time	4	107.5	26.875	0.74	0.61
	Sal*Time	4	49.3	12.325	0.34	0.84
	Error	4	145.7	36.425		
	Total	19	2601.8			
			<i>Rangia cuneata</i>			
Corpus Christi	Model	11	893.3	81.209	113.64	0.23
	Exp	1	196.0	196.000	6.41	0.31
	Sal	1	126.8	126.800	4.14	0.18
	Time	3	331.4	110.467	3.61	0.22
	Exp*Sal	1	2.1	2.100	0.07	0.82
	Exp*Time	3	181.5	60.500	1.98	0.35
	Sal*Time	2	55.5	27.750	0.91	0.52
	Error	2	61.2	30.583		
	Total	13	954.5			

(Continued)

Table A7 (Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula			<i>Rangia cuneata</i>			
	Model	4	38.5	9.625	0.15	0.95
	Exp	1	10.1	10.100	0.15	0.72
	Time	3	28.4	9.467	0.14	0.93
	Error	3	196.4	65.458		
	Total	7	234.9			
Ashtabula			<i>Palaemonetes kadiakensis</i>			
	Model	4	1726.5	431.625	10.67	0.04
	Exp	1	561.1	561.100	13.87	0.03
	Time	3	1165.4	388.467	9.60	0.05
	Error	3	121.4	40.458		
	Total	7	1847.9			
Texas City			<i>Palaemonetes pugio</i>			
	Model	14	1115.8	79.704	8.00	0.06
	Exp	1	453.7	453.700	43.55	0.007
	Sal	1	182.3	182.300	17.50	0.02
	Time	4	243.4	60.850	5.84	0.09
	Exp*Sal	1	210.2	210.200	20.18	0.02
	Exp*Time	4	9.9	2.475	0.24	0.90
	Sal*Time	3	16.3	5.433	0.52	0.70
	Error	3	31.2	10.400		
	Total	17	1147.0			
	Model	11	3320.3	301.845	14.69	0.07
Corpus Christi	Exp	1	1036.0	1036.000	57.29	0.02
	Sal	1	36.8	36.800	2.03	0.29
	Time	3	1110.4	370.133	20.47	0.05
			(Continued)			

Table A7 (Zn, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Corpus Christi			<i>Palaeomonetes pugio</i>			
	Exp*Sal	1	80.1	80.100	4.43	0.17
	Exp*Time	3	335.5	111.833	6.19	0.14
	Sal*Time	2	721.5	360.750	19.95	0.05
	Error	2	36.2	18.100		
	Total	13	3356.5			
Texas City			<i>Neanthes arenaceodentata</i>			
	Model	5	4569.5	913.900	4.58	0.08
	Exp	1	168.1	168.100	0.84	0.41
	Time	4	4401.4	1100.350	5.52	0.06
	Error	4	797.4	199.400		
	Total	9	5366.9			
Corpus Christi (First Run)	Model	5	217734.5	43546.900	4.36	0.09
	Exp	1	181980.1	181980.100	18.21	0.01
	Time	4	35754.4	8938.600	0.89	0.54
	Error	4	39966.4	9994.100		
	Total	9	257710.9			
Corpus Christi (Second Run)	Model	4	11414.5	2853.600	0.39	0.81
	Exp	1	7381.1	7381.130	1.00	0.39
	Time	3	4033.4	1344.460	0.18	0.90
	Error	3	22137.4	7379.100		
	Total	7	33551.9			

(Continued)

Table A7 (Zn, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula			<i>Tubifex</i> sp.			
	Model	5	7820.8	1564.160	10.23	0.02
	Exp	1	1904.4	1904.400	12.46	0.02
	Time	4	5916.4	1479.100	9.67	0.02
	Error	4	611.6	152.900		
	Total	9	8432.4			

Table A8
Analysis of Chromium Uptake
by Species Exposed to Various Sediments
Short-Term Studies

<u>Sediment</u>	<u>Source</u>	<u>df</u>	<u>Sum of Squares</u>	<u>M.S.</u>	<u>F</u>	<u>P>F</u>
Texas City			<i>Rangia cuneata</i>			
	Model	15	39.6	2.638	2.97	0.15
	Exp	1	0.2	0.220	0.25	0.64
	Sal	1	31.0	31.000	34.91	0.002
	Time	4	3.2	0.808	0.91	0.53
	Exp*Sal	1	0.8	0.800	0.86	0.41
	Exp*Time	4	0.4	0.095	0.11	0.46
	Sal*Time	4	4.0	0.992	1.12	0.46
	Error	4	3.6	0.888		
	Total	19	43.2			
Corpus Christi	Model	11	3.4	0.310	0.75	0.70
	Exp	1	0.4	0.380	1.08	0.41
	Sal	1	0.5	0.520	1.46	0.35
	Time	3	0.9	0.300	0.85	0.58
	Exp*Sal	1	0.0	0.000	0.00	0.97
	Exp*Time	3	0.7	0.227	0.64	0.66
	Sal*Time	2	0.9	0.465	1.31	0.43
	Error	2	0.7	0.356		
	Total	13	4.1			

(Continued)

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TEXAS A AND M RESEARCH FOUNDATION COLLEGE STATION
F/G 6/3
AVAILABILITY OF SEDIMENT-ADSORBED HEAVY METALS TO BENTHOS WITH --ETC(U)
AUG 78 J W NEFF, R S FOSTER, J F SLOWEY DACW39-75-C-0096

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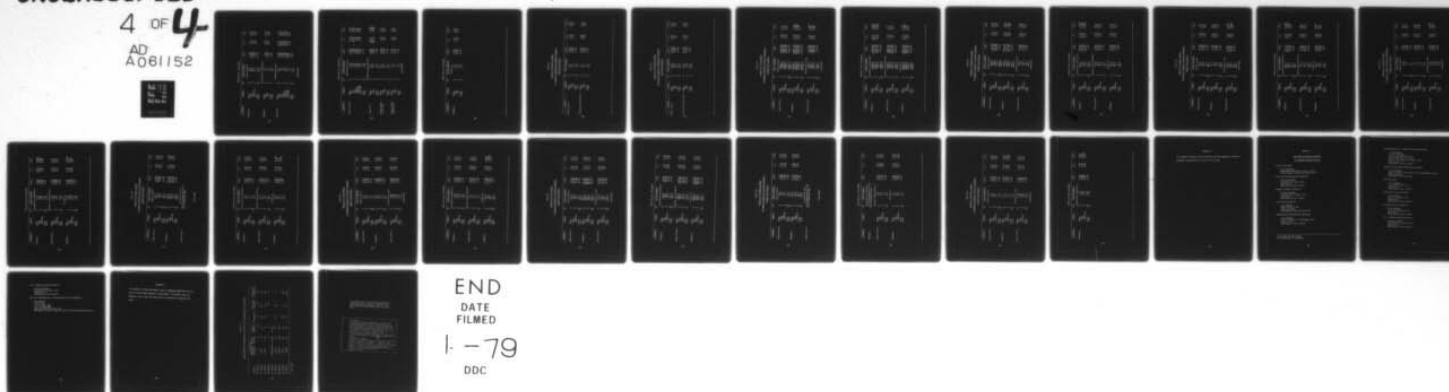


Table A8 (Cr, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula			<i>Rangia cuneata</i>			
	Model	10	99.9	9.990	1.51	0.26
	Exp	1	23.6	23.600	3.48	0.09
	Time	5	58.4	11.680	1.72	0.21
	Exp*Time	4	17.9	4.475	0.66	0.63
Ashtabula	Error	11	74.5	6.776		
	Total	21	174.4			
			<i>Palaemonetes kadiakensis</i>			
	Model	4	5.7	1.427	5.52	0.10
	Exp	1	1.1	1.100	4.35	0.13
Texas City	Time	3	4.6	1.533	5.91	0.09
	Error	3	0.8	0.258		
	Total	7	6.5			
			<i>Palaemonetes pugio</i>			
	Model	14	10.2	7.307	31.41	0.01
Texas City	Exp	1	2.9	2.900	106.52	0.002
	Sal	1	1.0	1.000	38.50	0.01
	Time	4	2.9	0.725	26.60	0.01
	Exp*Sal	1	0.6	0.600	22.01	0.018
	Exp*Time	4	2.5	0.625	23.25	0.01
	Sal*Time	3	0.2	0.067	2.83	0.21
	Error	3	0.1	0.027		
	Total	17	10.3			

(Continued)

Table A8 (Cr, Continued)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Corpus Christi	<i>Palaeomonetes pugio</i>					
	Model	11	1.83	0.166	15.12	0.06
	Exp	1	0.04	0.040	3.02	0.22
	Sal	1	1.63	1.630	135.39	0.007
	Time	3	0.07	0.023	1.88	0.37
	Exp*Sal	1	0.04	0.040	3.59	0.20
	Exp*Time	3	0.02	0.007	0.68	0.64
	Sal*Time	2	0.03	0.015	1.34	0.43
	Error	2	0.02	0.010		
	Total	13	1.85			
Texas City	<i>Neanthes arenaceodentata</i>					
	Model	5	22.2	4.440	741.07	0.0001
	Exp	1	10.8	10.800	1802.67	0.0001
	Time	4	11.4	2.850	475.67	0.0001
	Error	4	0.0	0.006		
	Total	9	22.2			
	Model	5	42.3	8.454	1.04	0.50
	Exp	1	10.2	10.200	1.26	0.32
	Time	4	32.1	8.025	0.99	0.50
	Error	4	32.4	8.100		
Corpus Christi (First Run)	Total	9	74.7			
	Model	4	0.8	0.205	1.15	0.47
	Exp	1	0.1	0.110	0.63	0.48
	Time	3	0.7	0.237	1.32	0.41
	Error	3	0.5	0.180		
	Total	7	1.3			
	(Continued)					

Table A8 (Cr, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula	Model	5	<i>Tubifex</i> sp. 1.0 0.4 0.6 0.6 1.6	0.200	1.33	0.40
	Exp	1		0.400	2.67	0.18
	Time	4		0.150	1.00	0.50
	Error	4		0.150		
	Total	9				

Table A9
Analysis of Mercury Uptake
by Species Exposed to Ashtabula Sediment

Short-Term Studies

Species	Source	df	Sum of Squares	M.S.	F	P>F
<i>Rangia cuneata</i>	Model	6	0.3	0.045	2.51	0.20
	Exp	1	0.1	0.090	3.90	0.12
	Time	5	0.2	0.036	1.60	0.33
	Error	4	0.1	0.020		
	Total	10	0.4			
<i>Palaemonetes kadiakensis</i>	Model	5	0.2	0.042	2.58	0.23
	Exp	1	0.1	0.100	4.84	0.12
	Time	4	0.1	0.028	1.19	0.46
	Error	3	0.1	0.023		
	Total	8	0.3			

Table A10
Analysis of Vanadium Uptake
by Species Exposed to Ashtabula Sediment
Short-Term Studies

Species	Source	df	Sum of Squares	M.S.	F	P>F
<i>Rangia cuneata</i>	Model	6	108.0	18.000	1.94	0.27
	Exp	1	63.0	63.000	7.28	0.05
	Time	5	45.0	9.000	1.04	0.50
	Error	4	34.6	8.650		
	Total	10	142.6			
<i>Palaemonetes kadiakensis</i>	Model	5	113.6	22.720	3.19	0.18
	Exp	1	78.7	78.700	12.51	0.04
	Time	4	34.9	8.725	1.39	0.41
	Error	3	18.9	6.290		
	Total	8	132.5			

Table A11
Analysis of Iron Uptake
by Species Exposed to Various Sediments
Longer Term Studies

<u>Sediment</u>	<u>Source</u>	<u>df</u>	<u>Sum of Squares</u>	<u>M.S.</u>	<u>F</u>	<u>P>F</u>
Corpus Christi			<i>Rançia cuneata</i>			
	Model	9	457882.3	50875.810	1.92	0.11
	Exp	1	70956.0	70956.030	2.68	0.12
	Time	4	250097.5	62524.367	2.37	0.09
	Exp*Time	4	136828.8	34207.200	1.29	0.31
Ashtabula	Error	20	528674.7	26433.730		
	Total	29	986557.0			
	Model	11	3736899.1	339718.100	7.09	0.0001
	Exp	1	735415.0	735414.970	15.91	0.0007
	Time	5	2392795.4	478559.080	10.35	0.0001
Corpus Christi	Exp*Time	5	608688.8	121737.760	2.63	0.05
	Error	21	970556.2	46216.960		
	Total	32	4707455.3			
			<i>Palaemonetes pugio</i>			
	Model	11	57789.2	5253.568	6.10	0.0003
Corpus Christi	Exp	1	5564.7	5564.690	6.66	0.02
	Time	5	24943.0	4988.604	5.97	0.002
	Exp*Time	5	27281.5	5456.308	6.53	0.001
	Error	19	15874.3	835.490		
	Total	30	73663.5			

(Continued)

Table A11 (Fe, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula	<i>Palaeomonetes kadiakensis</i>					
	Model	11	357460.8	32496.436	33.54	0.0001
	Exp	1	131312.0	131312.030	128.57	0.0001
	Time	5	93583.6	18716.710	18.33	0.0001
	Exp*Time	5	132565.2	26513.044	25.96	0.0001
	Error	22	22469.0	1021.320		
Corpus Christi	Total	33	379929.8			
	<i>Neanthes arenaceodentata</i>					
	Model	7	157398.9	22485.552	2.14	0.19
	Exp	1	28050.0	28050.050	2.40	0.17
	Time	3	61733.9	20577.966	1.76	0.25
	Exp*Time	3	67614.9	22538.303	1.93	0.23
Ashtabula	Error	6	70094.5	11682.420		
	Total	13	227493.4			
	<i>Tubificex sp.</i>					
	Model	9	678755.2	75417.250	6.75	0.003
	Exp	1	299880.0	299880.000	26.82	0.0004
	Time	4	229670.0	57417.500	5.14	0.02
Ashtabula	Exp*Time	4	149205.2	37301.300	3.34	0.06
	Error	10	111800.5	11180.050		
	Total	19	790555.7			

Table A12
Analysis of Manganese Uptake
by Species Exposed to Various Sediments
Longer Term Studies

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Corpus Christi	Model	9	6689.0	743.220	1.44	0.24
	Exp	1	1512.3	1512.300	2.94	0.10
	Time	4	2782.8	695.700	1.35	0.29
	Exp*Time	4	2393.9	598.468	1.16	0.36
	Error Total	20	10300.0	515.00		
Ashtabula		29	16989.0			
	Model	11	23753.6	14308.988	4.54	0.001
	Exp	1	114.5	114.170	0.24	0.63
	Time	5	12069.9	2413.978	5.06	0.003
	Exp*Time	5	11569.5	2313.908	4.85	0.004
Corpus Christi	Error Total	21	10011.0	476.710		
		32	33764.6			
	Model	11	446.9	40.628	3.64	0.005
	Exp	1	9.6	9.650	0.86	0.36
	Time	5	347.5	69.504	6.21	0.001
Corpus Christi	Exp*Time	5	89.7	17.948	1.60	0.20
	Error	22	246.4			
	Total	33	693.3	11.200		

(Continued)

Table A12 (Mn, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula	<i>Palaemonetes kadiakensis</i>					
	Model	11	1432.9	130.260	21.45	0.0001
	Exp	1	214.2	214.200	34.51	0.0001
	Time	5	713.8	142.770	23.00	0.0001
	Exp*Time	5	504.8	100.962	16.27	0.0001
Corpus Christi	Error	22	136.5	6.210		
	Total	33	1569.4			
	<i>Neanthes arenaceodentata</i>					
	Model	7	116.9	16.697	3.60	0.07
	Exp	1	32.8	32.770	6.30	0.05
Ashtabula	Time	3	38.6	12.857	2.47	0.16
	Exp*Time	3	45.5	15.180	2.92	0.12
	Error	6	31.2	5.210		
	Total	13	148.1			
	<i>Tubifex sp.</i>					
Ashtabula	Model	9	287.2	31.910	1.78	0.19
	Exp	1	57.8	57.800	3.23	0.10
	Time	4	218.7	54.675	3.05	0.07
	Exp*Time	4	10.7	2.675	0.15	0.96
	Error	10	179.0	17.900		
	Total	19	466.2			

Table A13

Analysis of Copper Uptake
by Species Exposed to Various Sediments

Longer Term Studies

<u>Sediment</u>	<u>Source</u>	<u>df</u>	<u>Sum of Squares</u>	<u>M.S.</u>	<u>F</u>	<u>P>F</u>
Corpus Christi			<i>Rangia cuneata</i>			
	Model	9	182.5	20.280	1.05	0.44
	Exp	1	16.1	16.130	0.83	0.37
	Time	4	135.9	33.968	1.76	0.18
	Exp*Time	4	30.5	7.632	0.39	0.81
Ashtabula	Error	20	386.7	19.330		
	Total	29	569.2			
	Model	11	81.3	7.395	0.44	0.92
	Exp	1	0.3	0.310	0.02	0.89
	Time	5	80.2	16.042	0.94	0.47
Corpus Christi	Exp*Time	5	0.8	0.166	0.01	1.00
	Error	21	356.9	16.993		
	Total	32	438.2			
			<i>Palaeomonetes pugio</i>			
	Model	11	922.2	83.835	4.05	0.0025
Corpus Christi	Exp	1	144.2	144.230	6.82	0.02
	Time	5	667.9	133.580	6.32	0.0009
	Exp*Time	5	110.1	22.012	1.04	0.42
	Error	22	465.3	21.151		
	Total	33	1387.5			

(Continued)

Table A13 (Cu, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula			<i>Palaemonetes kadiakensis</i>			
	Model	11	2654.4	241.312	5.39	0.0004
	Exp	1	955.1	955.100	20.27	0.0002
	Time	5	1417.4	283.478	6.02	0.0012
	Exp*Time	5	281.9	56.388	1.20	0.34
	Error	22	1036.7	47.121		
Corpus Christi	Total	33	3691.1			
			<i>Neanthes arenaceodentata</i>			
	Model	7	473.4	67.631	0.95	0.53
	Exp	1	1.8	1.800	0.02	0.88
	Time	3	440.2	146.737	1.97	0.22
	Exp*Time	3	31.4	10.470	0.14	0.93
Ashtabula	Error	6	447.0	74.500		
	Total	13	920.4			
			<i>Tubifex sp.</i>			
	Model	9	166.2	18.470	3.48	0.032
	Exp	1	16.2	16.200	3.06	0.11
	Time	4	114.2	28.550	5.39	0.01
	Exp*Time	4	35.8	8.950	1.69	0.23
	Error	10	53.0	5.300		
	Total	19	219.2			

Table A14
Analysis of Cadmium Uptake
by Species Exposed to Various Sediments
Longer Term Studies

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Corpus Christi			<i>Rangia cuneata</i>			
	Model	9	4.6	0.512	1.69	0.16
	Exp	1	0.05	0.050	0.16	0.70
	Time	4	2.9	0.715	2.36	0.09
	Exp*Time	4	1.7	0.425	1.40	0.27
Ashtabula	Error	20	6.1	0.304		
	Total	29	10.7			
	Model	11	7.7	0.696	2.83	0.02
	Exp	1	0.3	0.330	1.24	0.28
	Time	5	3.1	0.616	2.31	0.08
Corpus Christi	Exp*Time	5	4.2	0.850	3.19	0.03
	Error	21	5.6	0.266		
	Total	32	13.3			
			<i>Palaemonetes pugio</i>			
	Model	11	0.25	0.023	5.24	0.0006
Corpus Christi	Exp	1	0.01	0.010	3.05	0.10
	Time	5	0.19	0.038	9.78	0.0001
	Exp*Time	5	0.05	0.010	2.44	0.07
	Error	21	0.09	0.004		
	Total	32	0.34			

(Continued)

Table A14 (Cd, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula	<i>Palaemonetes kadiakensis</i>					
	Model	11	0.13	0.018	8.90	0.0001
	Exp	1	0.06	0.060	43.96	0.0001
	Time	5	0.04	0.008	5.45	0.002
	Exp*Time	5	0.03	0.006	4.04	0.001
Corpus Christi	Error	22	0.03	0.001		
	Total	33	0.16			
	<i>Neanthes arenaceodentata</i>					
	Model	7	2.20	0.314	0.43	0.85
	Exp	1	0.01	0.008	0.01	0.93
Ashtabula	Time	3	2.00	0.666	0.79	0.54
	Exp*Time	3	0.19	0.063	0.07	0.97
	Error	6	5.09	0.848		
	Total	13	7.29			
	<i>Tubifex sp.</i>					
Ashtabula	Model	9	0.31	0.035	11.06	0.0004
	Exp	1	0.00	0.003	1.07	0.32
	Time	4	0.28	0.070	22.00	0.0001
	Exp*Time	4	0.03	0.008	2.62	0.10
	Error	10	0.03	0.003		
	Total	19	0.34			

Table A15
Analysis of Nickel Uptake
by Species Exposed to Various Sediments
Longer Term Studies

<u>Sediment</u>	<u>Source</u>	<u>df</u>	<u>Sum of Squares</u>	<u>M.S.</u>	<u>F</u>	<u>P>F</u>
Corpus Christi			<i>Rangia cuneata</i>			
	Model	9	242.7	26.970	1.05	0.44
	Exp	1	50.7	50.700	1.97	0.18
	Time	4	163.5	40.882	1.59	0.22
	Exp*Time	4	28.5	7.118	0.28	0.89
Ashtabula	Error	20	514.7	25.730		
	Total	29	757.4			
	Model	11	1421.6	129.235	3.67	0.005
	Exp	1	216.4	216.420	5.95	0.02
	Time	5	487.0	97.392	2.66	0.05
Corpus Christi	Exp*Time	5	718.2	143.640	3.96	0.01
	Error	22	798.4	36.292		
	Total	33	2220.0			
			<i>Palaemonetes pugio</i>			
			[Ni] below detection limit at all sampling times			

(Continued)

Table A15 (Ni, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula			<i>Palaemonetes kadiakensis</i>			
	Model	11	8.5	0.777	3.02	0.013
	Exp	1	0.2	0.160	0.62	0.44
	Time	5	7.1	1.428	5.53	0.002
	Exp*Time	5	1.2	0.250	0.97	0.46
Corpus Christi	Error	22	5.7	0.259		
	Total	33	14.2			
			<i>Neanthes arenaceodentata</i>			
	Model	7	23.7	3.391	1.68	0.27
	Exp	1	3.7	3.700	1.53	0.26
Ashtabula	Time	3	13.1	4.377	1.82	0.24
	Exp*Time	3	6.9	2.303	0.95	0.47
	Error	6	14.5	2.410		
	Total	13	38.2			
			<i>Tubifex sp.</i>			
Ashtabula	Model	9	30.0	3.333	9.70	0.0007
	Exp	1	0.6	0.610	1.78	0.21
	Time	4	8.1	2.025	5.92	0.01
	Exp*Time	4	21.2	5.300	15.47	0.0003
	Error	10	3.4	0.344		
	Total	19	33.4			

Table A16
Analysis of Lead Uptake
by Species Exposed to Various Sediments
Longer Term Studies

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Corpus Christi	Model	9	1.0	0.111	1.01	0.46
	Exp	1	0.0	0.040	0.37	0.55
	Time	4	0.7	0.175	1.59	0.22
	Exp*Time	4	0.3	0.075	0.59	0.67
	Error	20	2.2	0.110		
Ashtabula	Total	29	3.2			
	Model	11	14.6	1.327	1.59	0.17
	Exp	1	0.0	0.030	0.04	0.85
	Time	5	9.9	1.986	2.36	0.08
	Exp*Time	5	4.6	0.928	1.10	0.39
Corpus Christi	Error	21	17.7	0.842		
	Total	32	32.3			
Corpus Christi	Model	11	0.08	0.008	0.99	0.48
	Exp	1	0.00	0.005	0.62	0.44
	Time	5	0.06	0.012	1.56	0.21
	Exp*Time	5	0.02	0.004	0.49	0.78
	Error	22	0.19	0.009		
Corpus Christi	Total	33	0.27			

(Continued)

Table A16 (Pb, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula	<i>Palaemonetes kadiakensis</i>					
	Model	11	0.30	0.027	2.13	0.07
	Exp	1	0.07	0.070	5.18	0.03
	Time	5	0.10	0.020	1.44	0.25
	Exp*Time	5	0.13	0.026	1.90	0.14
	Error	20	0.27			
Corpus Christi	Total	31	0.57	0.014		
	<i>Neanthes arenaceodentata</i>					
	Model	7	1.0	0.143	0.99	0.51
	Exp	1	0.1	0.090	0.52	0.50
	Time	3	0.3	0.113	0.64	0.61
	Exp*Time	3	0.6	0.190	1.07	0.43
Ashtabula	Error	6	1.1	0.183		
	Total	13	2.1			
	<i>Tubifex sp.</i>					
	Model	9	101.3	11.249	6.78	0.003
	Exp	1	0.5	0.500	0.30	0.60
	Time	4	85.3	21.315	12.75	0.0006
Ashtabula	Exp*Time	4	15.5	3.870	2.31	0.13
	Error	10	16.7	1.672		
	Total	19	118.0			

Table A17
Analysis of Zinc Uptake
by Species Exposed to Various Sediments
Longer Term Studies

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Corpus Christi	Model	9	245.0	27.219	0.69	0.71
	Exp	1	67.5	67.500	1.71	0.21
	Time	4	122.8	30.700	0.78	0.55
	Exp*Time	4	54.7	13.668	0.35	0.84
	Error	20	787.3	39.367		
<i>Rangia cuneata</i>						
			1032.3			
Ashtabula	Model	11	2649.9	240.899	2.01	0.08
	Exp	1	340.9	340.890	3.15	0.09
	Time	5	1481.2	296.244	2.74	0.05
	Exp*Time	5	827.8	165.556	1.53	0.22
	Error	21	2274.5	108.310		
<i>Palaeomonetes pugio</i>						
			4924.4			
Corpus Christi	Model	11	933.6	84.870	2.66	0.02
	Exp	1	17.3	17.330	0.54	0.47
	Time	5	588.1	117.626	3.68	0.01
	Exp*Time	5	328.1	65.624	2.05	0.11
	Error	22	704.0	32.000		
			1637.6			

(Continued)

Table A17 (Zn, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula	<i>Palaemonetes kadiakensis</i>					
	Model	11	312.0	28.363	1.17	0.36
	Exp	1	108.3	108.330	4.27	0.05
	Time	5	108.8	21.752	0.86	0.52
	Exp*Time	5	94.9	18.980	0.75	0.60
	Error	22	558.3			
Corpus Christi	Total	33	870.3	25.378		
	<i>Neanthes arenaceodentata</i>					
	Model	7	3004.4	429.201	1.09	0.47
	Exp	1	1824.0	1824.050	4.99	0.07
	Time	3	267.3	89.110	0.24	0.86
	Exp*Time	3	913.0	304.343	0.83	0.52
Ashtabula	Error	6	2193.5	365.583		
	Total	13	5197.9			
	<i>Tubifex</i> sp.					
	Model	9	15459.0	1717.672	2.24	0.11
	Exp	1	3458.4	3458.450	4.50	0.06
	Time	4	8106.3	2026.575	2.64	0.10
Ashtabula	Exp*Time	4	3894.3	973.575	1.27	0.34
	Error	10	7677.5			
	Total	19	23136.5	767.750		

Table A18

Analysis of Chromium Uptake
by Species Exposed to Various Sediments
Longer Term Studies

<u>Sediment</u>	<u>Source</u>	<u>df</u>	<u>Sum of Squares</u>	<u>M.S.</u>	<u>F</u>	<u>P>F</u>
Corpus Christi			<i>Rangia cuneata</i>			
	Model	9	20.8	2.314	1.17	0.37
	Exp Time	1	0.7	0.680	0.34	0.57
	Exp*Time	4	12.5	3.125	1.57	0.22
	Error	4	7.6	1.900	0.96	0.45
Ashtabula	Total	20	39.7	1.986		
		29	60.5			
	Model	11	124.4	11.313	1.47	0.20
	Exp Time	1	6.2	6.160	0.86	0.36
	Exp*Time	5	54.0	10.790	1.51	0.23
Corpus Christi	Error	5	64.3	12.866	1.81	0.16
	Total	21	149.7	7.127		
		32	274.1			
			<i>Palaemonetes pugio</i>			
			[Cr] below detection limit at all sampling times			

(Continued)

Table A18 (Cr, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
<i>Palaemonetes kadiakensis</i>						
[Cr] below detection limits at all sampling times						
<i>Neanthes arenaceodentata</i>						
Corpus Christi	Model	7	0.6	0.087	2.03	0.20
	Exp	1	0.2	0.160	3.04	0.13
	Time	3	0.3	0.100	1.85	0.24
	Exp*Time	3	0.1	0.050	0.92	0.48
	Error	6	0.3	0.054		
	Total	13	0.9			
<i>Tubificex sp.</i>						
Ashtabula	Model	9	1.2	0.128	6.64	0.005
	Exp	1	0.2	0.200	9.54	0.01
	Time	4	0.2	0.042	2.03	0.17
	Exp*Time	4	0.8	0.195	9.32	0.003
	Error	9	0.2	0.021		
	Total	18	1.4			

Table A19
Analysis of Mercury Uptake
by Species Exposed to Various Sediments
Longer Term Studies

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Corpus Christi	Model	9	1.3	0.144	3.10	0.017
	Exp	1	0.0	0.030	0.73	0.40
	Time	4	0.8	0.208	4.44	0.01
	Exp*Time	4	0.4	0.110	2.35	0.09
	Error Total	20	0.9	0.046		
Ashtabula	Model	11	3.2	0.292	7.96	0.0001
	Exp	1	0.2	0.240	7.31	0.01
	Time	5	2.3	0.454	13.90	0.0001
	Exp*Time	5	0.7	0.140	4.28	0.008
	Error Total	21	0.7	0.033		
Corpus Christi	Model	11	0.05	0.005	0.59	0.81
	Exp	1	0.00	0.003	0.34	0.56
	Time	5	0.05	0.009	1.15	0.37
	Exp*Time	5	0.00	0.003	0.08	0.99
	Error Total	22	0.18	0.008		
			0.23			
(Continued)						

Table A19 (Hg, Concluded)

Sediment	Source	df	Sum of Squares	M.S.	F	P>F
Ashtabula			<i>Palaeomonetes kadiakensis</i>			
	Model	11	1.12	0.102	3.44	0.007
	Exp	1	0.04	0.040	1.24	0.28
	Time	5	1.01	0.202	6.79	0.0006
	Exp*Time	5	0.07	0.014	0.48	0.79
	Error	22	0.66	0.030		
	Total	33	1.78			

Appendix B

This appendix contains a brief outline of the non-sequential extraction procedures used during all or part of this study.

Appendix B

Individual Extraction Procedure

For Sediment Characterization

Interstitial Water

50 gm sediment*
centrifuge at 9000 rpm, 10 min., 2-4°C
filter (0.45 μ), acidify with HNO₃ to pH 2

Distilled Deionized Water Extraction

25-30 gm sediment
125-150 ml D.D. H₂O (1:5)**
shake 90 min.
centrifuge, filter, acidify

Ammonium Acetate Extraction

25-30 gm sediment
125-150 ml of 1N NH₄Ac (1:5)
shake 90 min.
centrifuge, filter, acidify

Acetic Acid Extraction

4 gm sediment
200 ml 1M Hac (1:50)
shake 90 minutes
centrifuge, filter, not acidified

Hydroxylamine Hydrochloride Extraction

4 gm sediment
200 ml .1M NH₂OH in 0.01M HNO₃ (1:50)
shake 30 min.
centrifuge, filter, acidify

*all weights are wet weight

**ratio sediment to extractant

Peroxide Digestion - Ammonium Acetate Extraction

1-2 gm sediment
7-8 ml of 30% H_2O_2
acidify with HNO_3 (5 drops)
heat at 85°C for 5 hr., cool
100 ml of 1N NH_4OH in 1% HNO_3 (1:50)
shake 90 min.
centrifuge, filter, acidify

Sodium Citrate-Sodium Dithionite Extraction

1-2 gm sediment
100 ml of 16% Na Citrate and 1.67% Na Dithionite (1:50)
shake overnight
centrifuge, filter, acidify

DTPA Extraction

10 gm sediment
50 ml DTPA extract (1:5)
shake 90 min.
centrifuge, filter, acidify

Hydrochloric Acid Extraction

10 gm sediment
50 ml of 0.1N HCl (1:5)
shake 90 min.
centrifuge, filter, acidify

Calcium Chloride Extraction

10 gm sediment
50 ml of 0.1M CaCl_2 (1:5)
shake 90 min.
centrifuge, filter, acidify

15‰ Sodium Chloride Extraction

25-30 gm sediment
125-150 ml of 1.5% NaCl (1:5)
shake 90 min.
centrifuge, filter, acidify

30‰ Sodium Chloride Extraction

25-30 gm sediment
125-150 ml of 3% NaCl (1:5)
shake 90 min.
centrifuge, filter, acidify

Nitric Acid-Hydrofluoric Acid-Fuming Nitric Acid Digestion

4 gm sediment
15 ml of HF
10 ml of HNO_3 , heat
8 ml of fuming HNO_3
wash and dilute with 20 ml H_2O
centrifuge, acidify, dilute to 100 ml with distilled deionized H_2O

Appendix C

This appendix contains EPA Region V and VI suggested guidelines for disposal of metal-laden sediments in open waters. Bulk metal levels of Ashtabula, Texas City, and Corpus Christi sediments are compared with these.

Appendix C

Suggested Bulk Sediment Metal Criteria for Dredged Material Disposal

Metal	EPA Region V			Ashtabula Sediment	EPA Region VI	Texas City Sediment	Corpus Christi Sediment
	Moderately Polluted	Heavily Polluted					
Cd (mg/kg)	-*	>6		4.8	<2	2.4	21
Cr (mg/kg)	25-75	>75		175	<100	188	82
Cu (mg/kg)	25-50	>50		37	<50	48	120
Hg (mg/kg)	-	>1		1.1	<1	0.6	18
Fe (mg/kg)	17,000-25,000	>25,000		27,300	-	-	-
Ni (mg/kg)	20-50	>50		52	<50	48	17
Mn (mg/kg)	300-500	>500		356	-	-	-
Pb (mg/kg)	40-60	>60		42	<50	41	316
Zn (mg/kg)	90-200	>200		315	<75	161	4,055

* - not given

In accordance with letter from DAEN-RDC, DAEN-ASI dated 22 July 1977, Subject: Facsimile Catalog Cards for Laboratory Technical Publications, a facsimile catalog card in Library of Congress MARC format is reproduced below.

Neff, Jerry W

Availability of sediment-adsorbed heavy metals to benthos with particular emphasis on deposit-feeding infauna / by Jerry W. Neff, Robert S. Foster, J. Frank Slowey, Texas A&M Research Foundation, College Station, Texas. Vicksburg, Miss. : U. S. Waterways Experiment Station : Springfield, Va. : available from National Technical Information Service, 1978.

xxvi, 286 p. : ill. ; 27 cm. (Technical report - U. S. Army Engineer Waterways Experiment Station ; D-78-42)

Prepared for Office, Chief of Engineers, U. S. Army, Washington, D. C., under Contract No. DACW 39-~~9~~-C-0096 (DMRP Work Unit No. 1D06)

References: p. 209-226.

1. Benthos. 2. Dredged material. 3. Heavy metals. 4. Invertebrates. 5. Pollutants. 6. Sediment. 7. Water pollution.

I. Foster, Robert S., joint author. II. Slowey, J. Frank, joint author. III. Texas. A & M University, College Station. Research Foundation. IV. United States. Army. Corps of Engineers.

V. Series: United States. Waterways Experiment Station, Vicksburg, Miss. Technical report ; D-78-42.

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